THE ELECTRICAL RESISTIVITIES OF SOME SEMICONDUCTORS AT HIGH PRESSURES

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Summary

The resistivities of B, I, TiS_2, TiS_3, $TiSe_2$, ZrS_2, ZrS_3, $ZrSe_2$, $ZrSe_3$, and $ZrTe_2$ have been measured at room temperature under static pressures between 1 and 40,000 atm. In every instance the resistivity decreased with increasing pressure, but the change was never great enough to render the materials metallic. The largest change was shown by iodine, whose resistivity dropped by a factor of 1000 at 40,000 atm.

Under explosive shock pressures of about 250,000 atm, sulphur and iodine were found to have very low resistances and were presumably metallic. In similar conditions ZrS_3 and anthracene remained semiconductors.

I. Introduction

The quantum theory of matter indicates that any material will become metallic if it is compressed to a very high density. This occurs when the kinetic energy of the electrons increases sufficiently to allow them to escape from the electric fields of their nuclei. Calculations show that the pressures needed to cause the complete breakdown of matter into a homogeneous mass of free electrons and nuclei are about 10^{10} atm (Chandrasekhar 1951) and are therefore well beyond the present range of experimental pressures. However, it appears that more moderate pressures can cause a reduction in the energy gap between the valence and conduction bands of an insulator until they overlap and the material shows metallic conduction. Understandably, semiconductors are the most likely substances to undergo this kind of transition since their energy gaps are already low. Bridgman (1927, 1935*a*, 1951, 1952) has examined a number of semiconductors and found that their resistances nearly always decrease with increasing pressure. There is clear evidence that tellurium becomes metallic at 44,000 atm (Bridgman 1952), and Ag_2S at 65,000 atm (Bridgman 1952), and there is less direct evidence that black phosphorus changes into a metallic form at about 40,000 atm (Keyes 1953) and bismuth at 25,000 atm (Likhter and Vereshchagin 1957). Moreover, it appears that several materials which are normally regarded as insulators develop high electrical conductivities when they are compressed in strong explosive shock waves (Alder and Christian 1956).

The present paper describes some measurements which have been made in the hope of detecting new metallic modifications of other semiconductors. The materials studied were the elements:

B, P, S, As, I,

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and the following chalcogenide compounds of Group IVA metals:

TiS_2, TiS_3, $TiSe_2$,* ZrS_2, ZrS_3, $ZrSe_2$, $ZrSe_3$, $ZrTe_2$.*

In addition, a few experiments were performed on the organic semiconductor anthracene.

Three techniques were used. In the first, the material was compressed as a thin wafer between two steel bosses. Under these conditions the pressure was only approximately hydrostatic and it was combined with a shear stress arising from the tendency of the material to be extruded from between the bosses. In the second method, the substance was packed into a thin axial hole in a polyethylene cylinder, and the cylinder was then compressed inside a well-fitting steel pressure vessel. The pressure here was very nearly hydrostatic. In the final method, a stick of high explosive was used to drive a strong shock wave into a block of the material containing built-in electrodes, and a fast oscillograph recorded the change in resistance during the period of the shock (about 1 μsec). Here, again, the pressure was nearly hydrostatic but unfortunately the temperature of the shocked material was quite uncertain. It was probably in the range 1000–2000°K.

II. Experimental

(a) *Apparatus and Procedure*

(i) *Linear Compression to 40,000 atm at Room Temperature (about 25°C).*—Figure 1(*a*) illustrates the apparatus used in these experiments. The specimen was initially in the form of a thin disk *A*, 0·5 mm thick and 5 mm in diameter, mounted between two truncated cones *B* made of glass-hard ball-race steel. These were supported by constraining sleeves *C* of a high tensile steel, and the whole arrangement was aligned in a polyethylene tube *D*. The apparatus was placed between the platens of a 25 ton four-column press and a thrust was applied to the cones. This caused some extrusion of the specimen until it reached an equilibrium thickness of about 0·1 mm at the highest applied pressure of 40,000 atm (the exact thickness was governed by the shear strength of the material). The thrust was then reduced in regular steps and the resistance at each step was measured on a Cambridge Instrument Co. D.C. Decade Bridge. The specimen was again compressed and resistance readings were taken with both rising and falling pressures. These values were usually within a few per cent. of the initial ones, showing that no further extrusion had occurred. The pressure at each step was calculcated from the known value of thrust, together with the areas of the flat surfaces of the cones. The corresponding resistivity was derived from the measured resistance, together with the final area and thickness of the specimen. All the materials obeyed Ohm's law, and there was no evidence of polarization or electrolysis.

After a few experiments with this apparatus the flat compressing faces of the cones were found to have become slightly distorted into shallow concavities. They were therefore reground, and in subsequent runs they remained flat.

* It is possible that these two compounds are metallic (McTaggart 1958), although their resistivities are rather high for true metals.

Evidently the ball-race steel, although already very hard, had yielded and undergone some work hardening in the initial runs (cf. Bridgman 1937).

(ii) *Hydrostatic Compression to 40,000 atm at Room Temperature (about 25 °C).*—This method made use of the fact that polyethylene is an excellent medium for transmitting hydrostatic pressures. It is very much easier to seal than a liquid, and some earlier experiments (David and Hamann 1956) have shown that it remains sufficiently plastic to transmit pressures of at least 40,000 atm.

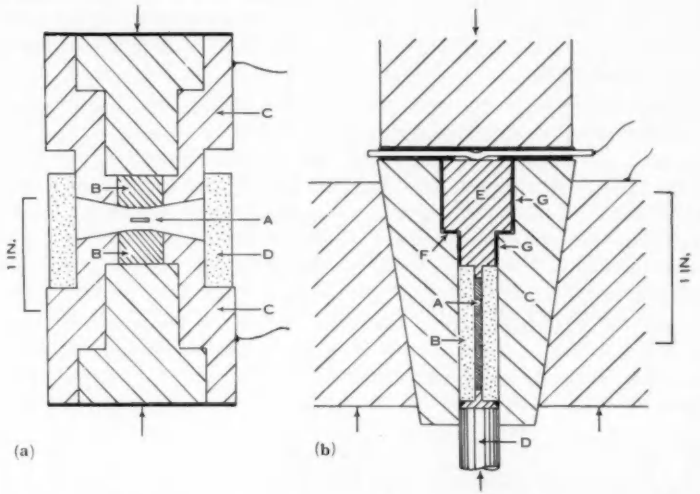

Fig. 1.—The experimental arrangements used in methods 1 and 2. The heavy lines indicate insulation.

The core of the apparatus is shown in Figure 1(*b*): it formed part of a high pressure intensifier which has been described elsewhere (Hamann 1957). The material was in the form of a pressed rod *A*, 1 mm in diameter and 20 mm long, held inside a polyethylene tube *B*. The tube was compressed in the steel vessel *C* by means of a "Carboloy"* piston *D*. The bottom of the rod was in electrical contact with the piston and pressure vessel, and the top was in contact with a hard steel plug *E*, insulated by a mica washer *F* and "Cellophane" tape *G*.

A preliminary measurement on a rod of cast bismuth gave the correct value for the resistivity, and a clear indication of the transition Bi(I)→Bi(II), occurring with a fourfold drop in resistance at 23,000 atm (Bridgman 1952). It showed that the electrical arrangement was satisfactory, and that the polyethylene was properly transmitting the pressure.

(iii) *Dynamic Compression by Explosive Shocks.*—This method was based on an arrangement used by Alder and Christian (1956). Its details have been

* Tungsten carbide cemented with cobalt.

published elsewhere (David and Hamann 1958*a*, 1958*b*). Essentially, it consisted in placing a block of the material on the top of a cylindrical charge of 60/40 RDX/TNT, and then detonating the explosive from the bottom. A detonation wave of about 250,000 atm pressure travelled up the charge and, at the top, drove a nearly planar shock wave into the specimen. About a microsecond later the shock front reached a pair of probes embedded in the material, 3 to 4 mm above the explosive, and wired in series with a charged electrolytic condenser and a carbon resistor. The shock caused a sudden reduction in the resistance of the material between the probes, and an increase in the current through the resistor. The corresponding rise in voltage was displayed as a vertical deflection of an oscillograph trace triggered by the detonation (for details see David and Hamann 1958*a*, 1958*b*).

Preliminary experiments with inert materials showed that some precautions were needed to avoid spurious signals caused by the ionization of the air near the probes. For instance, it was found that the air shock from the explosion produced quite a high conductance between bare probes inserted into the sides of the material. This could be greatly reduced by insulating the exposed parts of the wires and it could be eliminated if they were brought into the top of the specimen instead of the side. When these precautions were taken, materials such as polytetrafluoroethylene and *n*-heptane gave no sign of conduction.

In all the experiments the condenser and series resistor were mounted within a few inches of the specimen in order to reduce the inductance in the circuit. The series resistors had values of 71, 8·8, or 1 Ω, depending on the expected resistance of the shocked material.

(*b*) *Materials*

The chalcogenide compounds were kindly supplied by Mr. F. K. McTaggart, of this Division, who had prepared them and measured a number of their properties (McTaggart 1958). Of the elements, the boron was an electrolytic sample supplied by the Fairmount Co., Newark, N.J.; the sulphur and red phosphorus were from laboratory reagent stocks; the iodine was of analytical grade, and the arsenic was a spectroscopically pure specimen of the black form, supplied by Johnson, Matthey and Co., London. The anthracene was a purified sample kindly provided by Dr. I. G. Ross of the University of Sydney.

The specimens were formed in the following ways:

The pellets for the first kind of experiments, 1, were made by pressing the powdered materials between two steel pistons in a steel cylinder, under a compacting pressure of about 6000 atm. In most cases this treatment produced a hard coherent pellet with a density close to that of a single crystal. But boron failed to compact satisfactorily, probably because of its high shearing strength and its reluctance to self-weld (Bridgman 1935*b*).

The thin rods used in the method, 2, were formed by packing each powder tightly into its own polyethylene tube. For this operation the tube was constrained in a special steel ring, and a compacting pressure of about 1000 atm was applied by means of a drill rod.

The shock wave experiments, 3, required rather large specimens, about 15 mm in diameter and 20 mm high. In the case of sulphur these were readily prepared by casting, but the other materials had to be pressed into shape. The method was the same as that described above, 1, but the pelleting of the larger amounts involved greater frictional losses of pressure, so that the final densities were less than the theoretical. The difference was small for iodine and anthracene, which have low shearing strengths, but it amounted to about 25 per cent. for ZrS_3. Axial holes were drilled into the pellets to take stainless steel probes, 1 mm in diameter and 4 mm apart, terminating about 4 mm from the bottom.

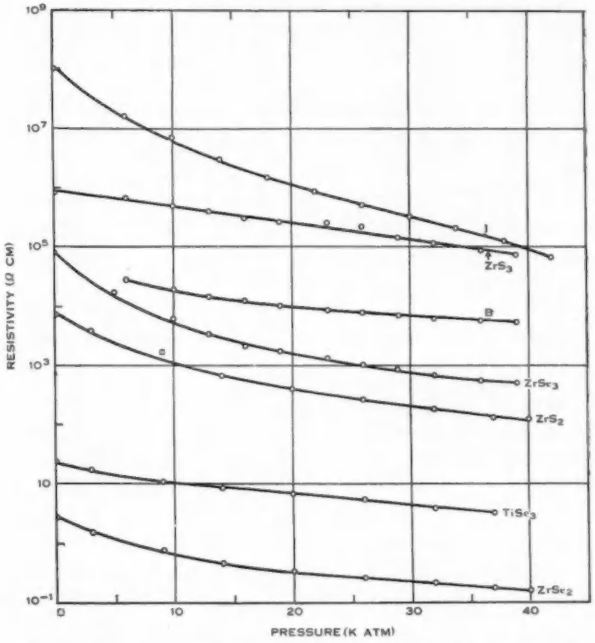

Fig. 2.—A logarithmic plot of resistivities measured by method 1.

III. Results

(*a*) *Method 1*

Figure 2 shows the results obtained with the apparatus in Figure 1(*a*). Considering first the chalcogenide compounds, we see that in every case the apparent resistivity decreased with increasing pressure. Part of the change may have been due to a purely mechanical increase in the area of contact between neighbouring grains in the pellet or between the pellet and the steel bosses. Some measurements on TiS_3 under more nearly hydrostatic conditions (see Fig. 3) showed a somewhat smaller fall in resistivity over the same pressure range. Also the absolute values of the resistivities were too great by factors between

2 and several hundred. This last effect is reminiscent of Bridgman's (1937) observation that a thin layer of bismuth, compressed by a similar method, had an apparent resistivity 2500 times greater than that of a rod of the same metal. He attributed the difference to the existence of a large surface resistance, but surprisingly he found that even under these conditions the transition Bi(I)→ Bi(II) at 23,000 atm was accompanied by the same percentage drop in *total* resistance as it was when the surface resistance was unimportant. Evidently, the conducting material in the surface layers was still bismuth itself. By analogy we can presume that the curves for the chalcogenide compounds in Figure 2 represent, at least qualitatively, the behaviour of the bulk materials.

It was mentioned earlier that boron showed a reluctance to bind into a coherent pellet, and the curve in Figure 2 can only be regarded as a rough indication of the behaviour of this element.

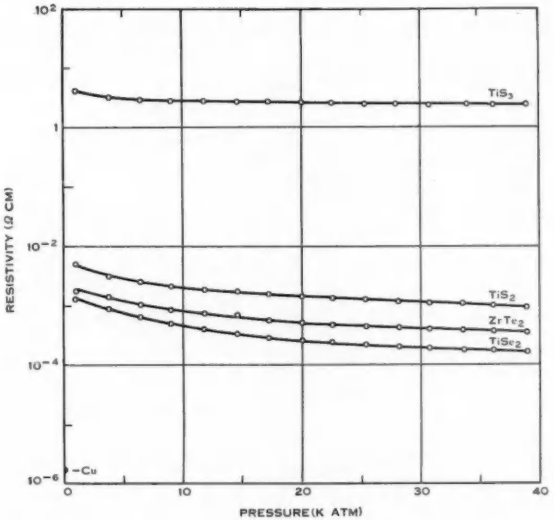

Fig. 3.—A logarithmic plot of resistivities measured by method 2.

On the other hand, iodine was readily deformed into a dense pellet and the measured value of its resistivity at 1 atm (*c.* 10^8 Ω cm) was sufficiently close to that of the bulk material (Moss 1952) to suggest that the interfacial resistance was small. It is therefore likely that the 1000-fold drop in resistivity observed between 1 and 40,000 atm was a genuine effect.

The experiments with red phosphorus and black arsenic failed because both materials changed irreversibly into denser allotropes above 10,000 atm. The phosphorus was partly transformed into the black modification (Bridgman 1914) and the arsenic into the " metallic " form. We are reminded here of the transformation of grey tin into metallic tin under pressure (Moss 1952).

(*b*) *Method 2*

Figure 3 shows the results of measurements made by this method. The favourable ratio of length to cross-sectional area of the specimens makes it likely that surface resistances were unimportant here, and the measured resistivities were close to the correct ones (McTaggart 1958). It should be noted that the resistivities plotted in Figures 2 and 3 are uncorrected for changes in the dimensions of the specimens under pressure. These corrections could only be made if the compressibilities of the materials were known, but they would in any case be small.

TABLE 1

SOME PROPERTIES OF SEMICONDUCTORS AT HIGH SHOCK PRESSURES

Material	Number of Experiments	Initial Density (g/cm^3)	Shock Velocity (m/sec)	Approx. Shock Pressure (atm)	Shock Resistance (Ω) between Electrodes Placed 3 to 4 mm from the Explosive
Sulphur ..	6	2·0	5200±500	230,000	<0·1
Iodine ..	7	4·9	3300±500	270,000	<0·1
ZrS_3 ..	4	2·6	3300±400	210,000	0·2
Anthracene..	2	1·2	(7500)*	(210,000)*	*c.* 100

* These values were based on one experiment only, and may be inaccurate.

(*c*) *Method 3*

In these experiments the initial resistance between the embedded electrodes was always more than a megohm. Table 1 lists the resistances in strong shock waves, together with the measured shock velocities and the corresponding pressures calculated from the relative shock impedances of the materials and of 60/40 RDX/TNT (Pack 1957).

Some additional experiments on sulphur (David and Hamann 1958*a*) showed that the shock *resistivity* was certainly less than 0·03 Ω cm.

IV. DISCUSSION

The experiments under static pressures showed a general decrease in resistivity with increasing pressure, but in no case was the change great enough to bring the material into the range of metallic conduction ($\rho < 10^{-4}\ \Omega$ cm), nor was there any sign of the abrupt drop in resistance which Mott (1956) has predicted for some kinds of semiconductors. The most striking behaviour was that of iodine (an intrinsic semiconductor with an energy gap of 1·3 eV (Moss 1952)), whose resistivity decreased by a factor of 1000 between 1 and 40,000 atm. An extrapolation of this trend would require iodine to become metallic at about 160,000 atm. But at some intermediate stage it must presumably collapse from a molecular crystal into an atomic one.

Under the higher pressures generated in the shock wave experiments, both sulphur and iodine had resistances which were indistinguishable from short

circuits in comparison with a 1 Ω series resistor. It is very likely that the materials were metallic under these conditions, although it is impossible to be absolutely sure of this without more definite knowledge of the shock resistivities or of the Hall effect in the shocked materials. Unfortunately, the necessary experiments would be extremely difficult.

It is a little surprising that ZrS_3, which might be expected to become metallic more readily than sulphur, had a measurable shock resistance. This anomaly may have been due to the fact that the material had been pressed to only 70 per cent. of its theoretical density, whereas the sulphur had been cast to its maximum density. The resistance of anthracene remained relatively high.

V. Acknowledgments

The author would like to thank Dr. I. W. Wark, Chief of the Division of Industrial Chemistry, for suggesting the measurements on the chalcogenide compounds, and Mr. F. K. McTaggart for providing the materials. He is also grateful to Mr. H. G. David for his help in the shock wave experiments, and to the Department of the Army for the facilities to carry them out.

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THE PHOTOCHEMICAL DECOMPOSITION OF THE CITRATE–FERRIC IRON COMPLEX: A STUDY OF THE REACTION PRODUCTS BY PAPER IONOPHORESIS

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Summary

A solution containing citric acid (0·1M) and ferric chloride (0·1M) was irradiated by bright sunlight for 3 hr. The products of the photochemical reaction were examined by means of paper ionophoresis using 0·05M sodium chloride as the electrolyte. Acetonedicarboxylic acid and acetoacetic acid separated readily and were identified by their positions on the paper and by their red-violet reactions on contact with a solution of ferric chloride sprayed onto the paper.

The ferrous iron simultaneously produced during the photochemical reaction also separated during ionophoresis and was identified on the paper.

The existence of an anionic citrate-ferric iron complex was demonstrated by paper ionophoresis.

I. INTRODUCTION

The photochemical decomposition of citric acid in the presence of ferric iron by ultraviolet light and by sunlight has long been known to result in the formation of acetone and carbon dioxide as the final products (Benrath 1910, 1911, 1912, 1917). Ciamician and Silber (1913) found that the same final products result also from the prolonged exposure of citric acid to light in the absence of ferric iron. Benrath (1911) reported that acetonedicarboxylic acid is probably an intermediate product in the decomposition catalyzed by ferric iron.

The ferric iron is simultaneously reduced to the ferrous state during the initial photochemical change which has been formulated (Benrath 1911; cf. Fry and Gerwe 1928; Rao and Aravamudan 1955) as follows:

$$\begin{array}{l} CH_2COOH \\ | \\ C(OH)COOH \\ | \\ CH_2COOH \end{array} + 2Fe^{3+} \rightarrow \begin{array}{l} CH_2COOH \\ | \\ CO \\ | \\ CH_2COOH \end{array} + CO_2 + 2Fe^{2+} + 2H^+. \quad \ldots\ (1)$$

The unstable acetonedicarboxylic acid would then decompose spontaneously to acetoacetic acid and carbon dioxide according to the equation:

$$\begin{array}{l} CH_2COOH \\ | \\ CO \\ | \\ CH_2COOH \end{array} \rightarrow \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_2COOH \end{array} + CO_2. \quad \ldots\ (2)$$

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Then the acetoacetic acid would break down to acetone and carbon dioxide as follows:

$$CH_3COCH_2COOH \rightarrow CH_3COCH_3 + CO_2. \quad \ldots\ldots\ldots\ldots \quad (3)$$

Ferric and ferrous iron form series of complexes with citrate (Hamm, Schull, and Grant 1954) and it has been established that citrate and the metal ion exist in these complexes in the ratio of 1 : 1 (Lanford and Quinan 1948; Bertin 1949; Warner and Weber 1953). Lanford and Quinan (1948) studied the citrate-ferric iron complex spectrophotometrically by the method of constant variations and concluded that $FeHCit^+$ was the form of the complex existing in highly acid solution. The results of pH titration experiments enabled Hamm, Schull, and Grant (1954) to extend the knowledge of this series of complexes which were formulated respectively as $FeHCit^+$, FeCit, $FeOHCit^-$, and $Fe(OH)_2Cit^{2-}$. Each was found to exist over a different range of pH.

The present work provides confirmation that the photochemical oxidation of citric acid by sunlight in the presence of ferric iron proceeds according to the above formulation. Separation of the intermediate products of the reaction was achieved by means of paper ionophoresis using 0·05M sodium chloride as the electrolyte.

Evidence is presented for the formation of at least one of the anionic citrate-ferric iron complexes identified by Hamm, Schull, and Grant (1954), but under the conditions of the ionophoresis no ferrous iron complex appeared to exist. Further, no ionophoretic evidence was obtained for the existence of the cationic citrate-ferric iron complex described by Lanford and Quinan (1948).

II. Experimental

(*a*) *The Photochemical Oxidation of Citric Acid in the Presence of Ferric Chloride*

Equal volumes (5 ml) of 0·2M citric acid and 0·2M ferric chloride solutions were mixed in a Pyrex test tube which was immersed in ice-water and left exposed to bright sunlight. Thus according to equation (**1**) the solution contained only sufficient ferric iron for the oxidation of one-half of the citric acid present.

The solution was yellow immediately after mixing but on standing in sunlight the colour gradually deepened and became red-brown due to the reaction of residual ferric iron with the intermediate products of the photochemical change. The colour reached a maximum intensity and then slowly faded until after irradiation for a total of about 3 hr the solution was colourless, indicating that the ferric iron had been reduced completely to the ferrous state.

Samples of the colourless solution were subjected to paper ionophoresis without delay.

(*b*) *Paper Ionophoresis*

The ionophoresis was performed on Whatman No. 4 paper using an apparatus of the type described by Foster (1952). The paper was completely wetted with the electrolyte for which 0·05M sodium chloride solution was used. Similar results were obtained when acetate buffer (pH 5·7) was substituted as the electrolyte for the separation of the intermediate products of the photochemical

reaction. 0·1M Nitric acid was used as the electrolyte in an attempt to confirm the existence of the cationic complex identified by Lanford and Quinan (1948).

The wetted paper was blotted and allowed to come to equilibrium in the apparatus with the electrolyte. The test solutions were applied by means of a platinum loop through a suitably perforated sheet of polyvinyl chloride placed between the paper and the upper glass plate. A solution containing caffeine (0·1M) and potassium *p*-nitrobenzenesulphonate (0·1M) was also applied to the starting-line of the paper, the caffeine to mark the extent of electroendosmotic flow and the *p*-nitrobenzenesulphonate ion to provide a standard of migration toward the anode (Frahn and Mills 1959). Table 1 presents M_N values of the various compounds examined. M_N value is defined as the ratio of the true distance of migration of the compound to the true distance of migration of *p*-nitrobenzenesulphonate ion.

TABLE 1

RELATIVE MOBILITIES OF COMPOUNDS DETECTED AFTER IONOPHORESIS IN 0·05M SODIUM CHLORIDE

Compound	M_N Value
Acetonedicarboxylic acid	1·64
Acetoacetic acid	1·15
Ethyl acetoacetate	0·00
Citric acid*	0·86
Citrate-iron(III) complex	1·44
Iron(III)†	0·12
Iron(II)	—1·39

* Applied as 0·02M solution.

† Adsorbed at origin.

Generally, ionophoresis was allowed to proceed for 30 min with a potential gradient of about 22 V/cm. After removal from the apparatus the paper was inspected, either while still wet with the electrolyte or after drying in the oven at 100 °C, in the light from an Hanovia Chromatolite ultraviolet lamp. Caffeine and *p*-nitrobenzenesulphonate were then detected as absorbing spots on the paper. Under the above conditions of ionophoresis, the true distance of migration of the *p*-nitrobenzenesulphonate ion was 7·8 cm.

(*c*) *Detection of the Separated Compounds*

For the detection of the unstable compounds, acetonedicarboxylic acid and acetoacetic acid, the paper, while still wet with electrolyte, was sprayed without delay with either 2M ferric chloride solution or with a solution containing chromic acid (1·2 per cent.) and potassium permanganate (0·6 per cent.) in 6N sulphuric acid (referred to in Section III (*a*) as concentrated chromic acid-permanganate reagent). After spraying with the latter reagent the paper was stored between glass plates for about 30 min during which reactive substances appeared as white spots on a brown ground. To obtain a permanent record the paper was

washed in 5 per cent. sodium carbonate solution and then in running tap-water for 15 min. It was finally dried in the oven at 100 °C.

The detection of the more stable compounds was facilitated by drying the paper in the oven for 10 min and then spraying with a solution containing chromic acid (0·2 per cent.) and potassium permanganate (0·1 per cent.) in 1·6N sulphuric acid (Frahn and Mills 1956, 1959) referred to in Section III (*c*) as dilute chromic acid-permanganate reagent. The paper was developed by storing between glass plates for 30 min. It was then washed and dried as described above to obtain a permanent record.

Ferrous iron was located by its bright blue reaction on the dried papers when these were sprayed with a solution of potassium ferricyanide (1 per cent.) in 1N hydrochloric acid (cf. Pollard 1954). Ferric iron was similarly located by spraying with potassium ferrocyanide (1 per cent.) in 1N hydrochloric acid. It was found that the latter reagent could be used also for the detection of ferrous iron which became partially oxidized to the ferric state in the process of oven-drying the paper.

Ferrous and ferric iron were also readily located as dark spots by viewing the paper in ultraviolet light before spraying for the chemical detection of iron (Pollard *et al.* 1957).

(*d*) *Reference Compounds*

Acetoacetic acid and acetonedicarboxylic acid were separately applied as *c.* 0·1M solutions to the starting-line of the paper strip to serve as reference compounds with which to compare the migrations of the intermediate products of the photochemical oxidation.

A *c.* 0·1M solution of acetoacetic acid was prepared by hydrolysing ethyl acetoacetate (0·13 g) in 0·1N sodium hydroxide (10 ml) for 1 hr at room temperature.

Acetonedicarboxylic acid was prepared according to the directions of Adams, Chiles, and Rassweiler (1946).

Citric acid (Hopkin and Williams Ltd., B.P. grade) was applied to the paper for reference as a 0·02M solution.

0·1M Solutions of ferrous ammonium sulphate and ferric chloride were separately applied to provide reference samples of both valence states of iron.

III. Results and Discussion

(*a*) *Separation of the Intermediate Products of the Photochemical Oxidation of Citric Acid*

The ferric chloride reagent which was sprayed onto the wet paper after ionophoresis reacted immediately with the reference samples of acetonedicarboxylic acid and acetoacetic acid to give strong red-violet spots (Ceresole 1882; Pechmann 1891) the M_N values of which are recorded in Table 1.

The sample of the experimental solution containing the products of the photochemical oxidation of citric acid was found to be resolved into two spots both of which gave red-violet reactions with the ferric chloride spray reagent.

The more intense spot was identified as acetonedicarboxylic acid by its position on the paper alongside the spot due to the authentic compound. The other spot, although much weaker, was easily perceptible and was identified as acetoacetic acid. The spots due to acetonedicarboxylic acid trailed faintly in each case and merged with those due to acetoacetic acid as indicated in Figure 1, lanes *f* and *h*. Evidently, acetonedicarboxylic acid progressively decomposed during the ionophoresis in accordance with the reaction represented by equation (**2**).

Another paper, after ionophoresis, was dried and heated in the oven at 100 °C for 10 min before spraying with the ferric chloride reagent. No red-violet spots appeared on this paper indicating that acetonedicarboxylic acid, acetoacetic acid, and the compounds separated from the experimental solution were easily destroyed under these conditions of heating. This provides further evidence for the identity of the latter compounds.

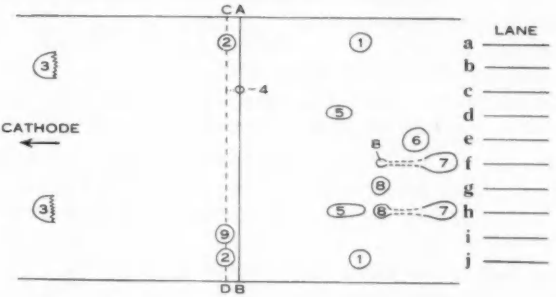

Fig. 1.—A diagram showing relative positions of compounds after electrophoresis in 0·05M sodium chloride. *AB* represents the starting-line and *CD* marks the extent of electroendosmotic flow as indicated by the position of caffeine. 1, *p*-Nitrobenzenesulphonate; 2, caffeine; 3, Fe^{2+}; 4, Fe^{3+}; 5, citric acid; 6, citrate-Fe^{3+} complex; 7, acetonedicarboxylic acid; 8, acetoacetic acid; 9, ethyl acetoacetate. Lane *h* indicates the separation of citric acid and the products of the photochemical oxidation.

On another paper these compounds were also located by using the concentrated chromic acid-permanganate reagent. The residual citric acid remaining after the reduction of the ferric iron originally present in the irradiated experimental solution was revealed on this paper as a third spot which had migrated more slowly than had either acetonedicarboxylic acid or acetoacetic acid. It was found, incidentally, that the M_N value of citric acid under these conditions of ionophoresis depends upon the concentration of the applied solution. The M_N value recorded in Table 1 is that of the 0·02M solution of citric acid previously specified. In more concentrated solutions citric acid exhibits greater M_N values, which however are difficult to assess with accuracy, because the spots become more elongated.

(b) Detection of Ferrous and Ferric Iron after Paper Ionophoresis

Ferrous iron resulting from the photochemical change was located on a dried paper after ionophoresis by spraying with the ferricyanide reagent. Ferrous iron from both the experimental and reference solutions yielded bright blue spots immediately and was shown to have migrated rapidly toward the cathode as expected.

By contrast the reference sample of ferric iron remained at the site of its application to the paper apparently strongly adsorbed on the filter paper fibres. It showed a slight tendency to streak towards the cathode. No ferric iron was detected in the experimental solution.

(c) Citrate-Ferric Iron Complex

The existence of an anionic citrate-ferric iron complex such as described by Hamm, Schull, and Grant (1954) was demonstrated as follows: A solution containing citric acid (0·1M) and ferric chloride (0·1M) which was prepared and stored in the dark was subjected to ionophoresis in 0·05M sodium chloride under the conditions described above except that light was excluded from the paper during ionophoresis. Samples of the solution were applied one on each half of the starting line and adjacent to each spot the reference solutions of citric acid and ferric chloride were separately applied. After ionophoresis the paper was dried in the oven and cut longitudinally into halves.

One-half of the paper was treated with the dilute chromic acid-permanganate reagent. The experimental solution provided a single nearly round white spot (M_N value=1·44) whereas the citric acid applied for reference was revealed as a more elongated slower-moving spot.

The other half of the paper was sprayed with the ferrocyanide reagent. The experimental solution yielded one bright blue spot (M_N value=1·44). The reference sample of ferric iron was revealed at the origin.

The fact that the citrate and ferric ions in the mixture migrated together during ionophoresis with an M_N value (1·44) different from those of either citrate (0·86) or ferric iron (0·12) alone is evidence for the existence of a strongly negatively charged citrate-ferric iron complex. This or a similar form of the complex was shown to exist also in moderately acidic solution by repeating the ionophoresis in acetate buffer (pH 4·0) as the electrolyte in place of 0·05M sodium chloride. The complex migrated as an anion, M_N value=1·37.

The solution used for these experiments contained equimolecular quantities of citric acid and ferric chloride. The fact that ionophoresis of this solution yielded only a single spot revealed by spraying with either the chromic acid-permanganate or the ferrocyanide reagents confirmed the conclusion of Lanford and Quinan (1948), Bertin (1949), and Warner and Weber (1953) that the ratio of citrate to ferric iron in the complex is unity. Further evidence was provided by ionophoresis of mixtures in which the citrate-ferric iron ratio was 1·1 and 0·9, respectively. In addition to the spots representing the complex these mixtures yielded extra spots corresponding with free citric acid in the first case and with free ferric iron in the other case.

An attempt was made to demonstrate the existence of the cationic form of the complex which exists when the solution is 0·08–0·15M in nitric acid and which was identified by Lanford and Quinan (1948) as $FeHCit^+$. Ionophoresis of a solution containing citric acid (0·1M) and ferric nitrate (0·1M) was conducted in the dark in 0·1M nitric acid as the electrolyte and was allowed to proceed for 1 hr with a potential gradient of approx. 7 V/cm.

After ionophoresis the paper was gently dried and examined in the light from the ultraviolet lamp for the detection of absorbing spots due to ferric iron. The citric acid-ferric nitrate mixture and ferric nitrate applied for reference each yielded one absorbing spot with identical M_N values (−1·71).

The paper strip was then treated with the dilute chromic acid-permanganate reagent. Single spots appeared for the citric acid-ferric nitrate mixture and for the reference sample of citric acid each with zero M_N value.

The mixture of citric acid and ferric nitrate was evidently resolved into its components under these conditions of ionophoresis. Therefore this experiment does not provide evidence for the existence in 0·1M nitric acid solution of a citrate-ferric iron complex.

IV. Acknowledgments

The author wishes to thank Dr. H. R. Marston for his interest in this work and Dr. J. A. Mills for helpful discussion and criticism.

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MAGNETIC MOMENTS OF COPPER(II) COMPLEXES

By Kazuo Ito* and Toshiko Ito†

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Summary

Magnetic moments of octahedral, tetrahedral, square planar, trigonal planar, and trigonal pyramidal Cu(II) complexes have been discussed theoretically including the orbital contribution on the basis of the molecular orbital theory. It has been shown that the orbital contribution of electrons to the magnetic moment is expected only in tetrahedral, trigonal planar, and trigonal pyramidal complexes. The effective magnetic moment of tetrahedral Cu(II) complexes has been estimated to be about 2·2 at room temperature and that of tri-coordinated Cu(II) complexes to be higher than the spin-only value. The hypothesis of electron promotion to a $4p$ level in Cu(II) complexes has been criticized.

I. Introduction

It is well known that the effective magnetic moments of coordination complexes can be interpreted in terms of the " spin-only " scheme in connection with the nature of the bonds and the configurations of these compounds, neglecting completely the residual orbital moments. In the case of Cu(II) complexes, however, the scheme fails to serve as a criterion for bond types or configurations in the compounds, predicting always 1·73 Bohr magnetons (B.M.) for every possible bond type and configuration. But Pauling (1940) suggested that, if the orbital contribution of electrons to the magnetic moment is taken into account, the moment value of the square Cu(II) complexes is expected to be slightly lower than that of its tetrahedral complexes because of the greater quenching effect of the more unsymmetrical ligand field in the former upon the residual orbital moment. In fact, Rây and Sen (1948) found that the magnetic moments of four-coordinated Cu(II) complexes fall into two groups, 1·66 to 1·81 and 1·90 to 2·20 B.M. More recently, Kishita, Muto, and Kubo (1957) have found that the magnetic moments of tri-coordinated Cu(II) complexes are rather lower than 1·73 at room temperature. Since the orbital contribution can not only increase the spin-only value in some cases but also decrease it in some other cases depending on the structures of complexes, it would be of some interest to investigate semiquantitatively for several structures the orbital contribution of electrons to the magnetic moment of Cu(II) coordination compounds. In the following, the magnetic moments of octahedral, tetrahedral, square planar, trigonal planar, and trigonal pyramidal Cu(II) complexes are discussed including the orbital contribution on the basis of the method developed by Kotani (1949).

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II. Theory

Suppose that a g_n-fold degenerate level n is split into sublevels by an external magnetic field H and the energy of the sublevel is expressed as

$$E_{nm}=E_n^{(0)}+E_{nm}^{(1)}H+E_{nm}^{(2)}H^2+\ldots, \quad \ldots\ldots\ldots \quad (1)$$

where m denotes the numbering of the sublevel. Then, the magnetic susceptibility X is given by (Van Vleck 1932)

$$X_{\mathrm{mol}}=N\frac{\sum_{n,m}[(E_{nm}^{(1)})^2/kT-2E_{nm}^{(2)}]\mathrm{e}^{-E_n^{(0)}/kT}}{\sum_n g_n \mathrm{e}^{-E_n^{(0)}/kT}}. \quad \ldots\ldots\ldots \quad (2)$$

In order to calculate E_{nm}, the Hamiltonian for a central metallic ion is taken as (Kotani 1949)

$$=H^0+V_{\mathrm{ligand}}+A\sum_i l_i s_i+\beta H(L+2S), \quad \ldots\ldots\ldots \quad (3)$$

where V_{ligand} is the potential energy due to a ligand field, i the numbering of electrons, $A\sum_i l_i s_i$ spin-orbit interaction, β the Bohr magneton, the last term denotes energy due to an external magnetic field, and $H^0+A\sum_i l_i s_i$ the Hamiltonian of the free metallic ion.

(a) *Octahedral Cu(II) Complex*

In the case of an octahedral complex, a fivefold degenerate $3d$ level is split under the ligand field of 0_h symmetry into two sublevels, a stable threefold degenerate (d_{xy}, d_{yz}, and d_{zx}) level and an unstable twofold degenerate (d_{z^2} and $d_{x^2-y^2}$) level (Van Vleck 1935 ; Kuroda and Ito 1955). These levels are occupied by nine electrons of a Cu(II) ion as shown in Figure 1. Since 10 electrons make

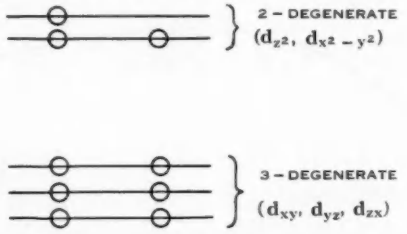

Fig. 1.—The ground state of Cu(II) under a ligand field of 0_h symmetry.

the system into a closed-shell configuration, E_{nm} in equation (1) can be calculated (Kotani 1949) in terms of a hole instead of nine real electrons. Thus, the energy level of the ground state shown in Figure 1 is fourfold degenerate and its states are expressed including spin as $d_{z^2}\alpha$, $d_{z^2}\beta$, $d_{x^2-y^2}\alpha$, and $d_{x^2-y^2}\beta$, respectively, in terms of a hole. However, the degenerate level is not affected by spin-orbit interaction and, therefore, there is no orbital contribution to the magnetic moment in the present case because the integrals $\int d_{z^2}H\cdot Ld_{z^2}\alpha\tau$ etc. are zero.

(b) Tetrahedral Cu(II) Complex

In this case, a fivefold degenerate 3*d* level is split by V_{ligand} of T_d symmetry into two sublevels and occupied by nine electrons as shown in Figure 2. The energy level of the ground state shown in Figure 2 is sixfold degenerate and its

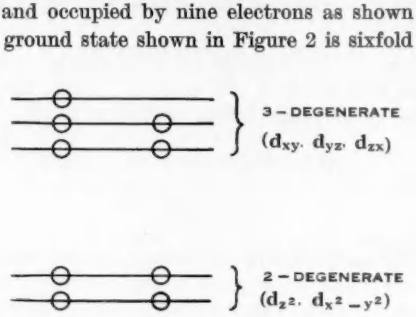

Fig. 2.—The ground state of Cu(II) under a ligand field of T_d symmetry.

states are expressed as $d_{xy}\alpha$, $d_{xy}\beta$, $d_{yz}\alpha$, $d_{yz}\beta$, $d_{zx}\alpha$, and $d_{zx}\beta$, respectively, in terms of a hole. E_{nm} and effective magnetic moment $\mu_{\text{eff.}}$ for the present case can be obtained from Kotani's (1949) results, the latter being given by

$$\mu^2_{\text{eff.}}=(3x+8-8e^{-3x/2})/x(1+2e^{-3x/2}), \quad \ldots\ldots\ldots \quad (4)$$

where $x=A/kT$. The behaviour of (4) is shown in Figure 3. Since the value

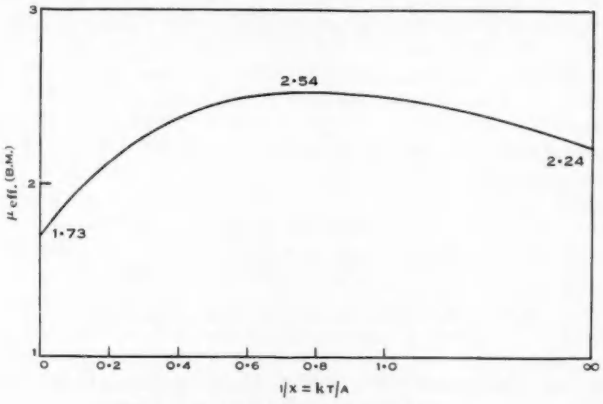

Fig. 3.—The behaviour of equation (4).

of A for a Cu(II) ion is about 800 cm^{-1} ($x=A/kT$ is about 4 at room temperature; Condon and Shortley 1951), the magnetic moments of tetrahedral Cu(II) complexes are expected to be around 2·2 at room temperature including the orbital contribution.

(c) *Square Planar Cu(II) Complex*

In this case, a fivefold degenerate $3d$ level is split by V_{ligand} of D_{4h} symmetry into four sublevels and occupied by nine electrons as shown in Figure 4. Since the ground state has no orbital degeneracy, the orbital contribution is zero (Kotani 1949) for the present case.

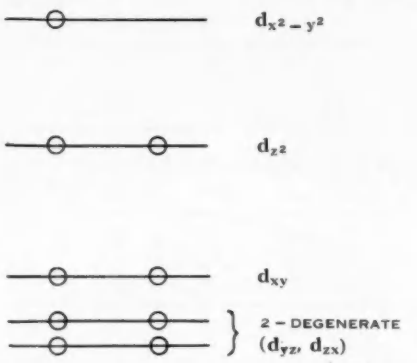

Fig. 4.—The ground state of Cu(II) under a ligand field of D_{4h} symmetry.

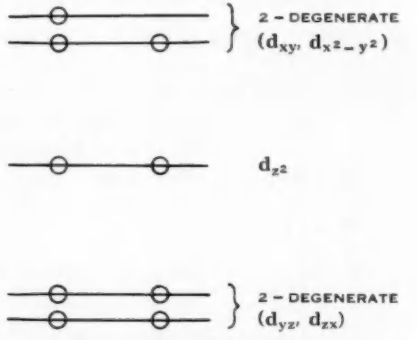

Fig. 5.—The ground state of Cu(II) under a ligand field of D_{3h} symmetry.

(d) *Trigonal Planar Cu(II) Complex*

In this case, a fivefold degenerate $3d$ level is split by V_{ligand} of D_{3h} symmetry into three sublevels and occupied by nine electrons as shown in Figure 5. The coordinate system for Figure 5 is given in Figure 6. The energy level of the ground state shown in Figure 5 is fourfold degenerate including spin. Spin-orbit interaction splits the level into two and each of these is further split into two

by an external magnetic field. The energy values of these levels are given, in the form of (**1**), by :

(i) $H_z \neq 0$, $H_x = H_y = 0$

n	m	$E^{(0)}$	$E^{(1)}$	$E^{(2)}$
2	2	A	β	0
	1	A	$-\beta$	0
1	2	$-A$	3β	0
	1	$-A$	-3β	0

(ii) $H_x \neq 0$, $H_y = H_z = 0$; $H_y \neq 0$, $H_x = H_z = 0$

n	m	$E^{(0)}$	$E^{(1)}$	$E^{(2)}$
2	2	A	β	0
	1	A	$-\beta$	0
1	2	$-A$	β	0
	1	$-A$	$-\beta$	0

The effective magnetic moment is given by

$$\mu^2_{\text{eff.}} = (11 + 3e^{-2x})/(1 + e^{-2x}). \quad \ldots\ldots\ldots\ldots \quad (5)$$

The behaviour of (**5**) is shown in Figure 7. Where $x = 4$, the magnetic moments

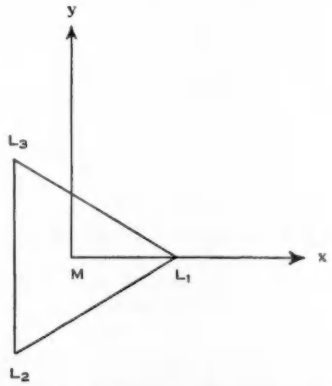

Fig. 6.—The coordinate system for Figure 5.

of trigonal planar Cu(II) complexes are expected to be about 3·3 at room temperature including the orbital contribution.

(*e*) *Trigonal Pyramidal Cu(II) Complex*

In this case, a fivefold $3d$ level is split by V_{ligand} of C_{3v} symmetry into three sublevels as shown in Figure 5. However, the sequence of these levels is not always the same as that shown in Figure 5, depending on the angle between ML_1 (ML_2 or ML_3) bond and $L_1L_2L_3$ plane (see Fig. 8). If the non-degenerate level is the highest one, there is no orbital contribution for the reason discussed in Section II(*c*).

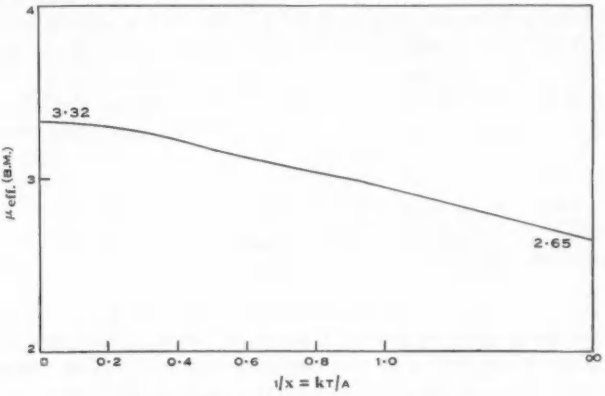

Fig. 7.—The behaviour of equation (5).

If, on the other hand, the angle between ML_1 (ML_2 or ML_3) bond and $L_1L_2L_3$ plane is around 45°, the degenerate level (d_{yz}, d_{zx}) may be the highest one. In such a case, the energy values of the levels split by spin-orbit interaction and an external magnetic field are given by :

(i) $H_z \neq 0$, $H_x = H_y = 0$

n	m	$E^{(0)}$	$E^{(1)}$	$E^{(2)}$
2	2	$A/2$	0	0
	1	$A/2$	0	0
1	2	$-A/2$	2β	0
	1	$-A/2$	-2β	0

(ii) $H_x \neq 0$, $H_y = H_z = 0$; $H_y \neq 0$, $H_x = H_z = 0$

n	m	$E^{(0)}$	$E^{(1)}$	$E^{(2)}$
2	2	$A/2$	β	0
	1	$A/2$	$-\beta$	0
1	2	$-A/2$	β	0
	1	$-A/2$	$-\beta$	0

The effective magnetic moment is given by

$$\mu^2_{\text{eff.}} = (6+2e^{-x})/(1+e^{-x}). \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

The behaviour of (6) is shown in Figure 9. When $x=4$, the magnetic moment of about 2·4 is expected for the case of (6) at room temperature.

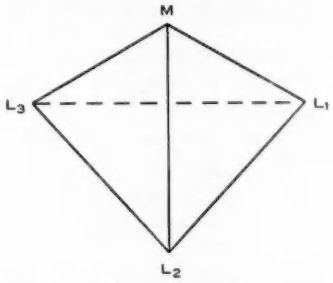

Fig. 8.—Trigonal pyramidal Cu(II) complex.

III. Discussion

The treatment given in Section II(*a*)–(*e*) is based on the molecular orbital theory and the configuration of nine electrons in a split 3*d* level is determined definitely for each case as presented in the figures. However, according to the atomic or hybridized orbital theory, the electron configurations would differ

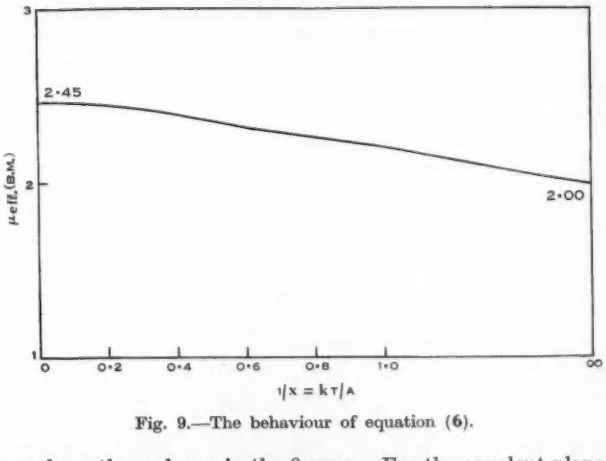

Fig. 9.—The behaviour of equation (6).

in some cases from those shown in the figures. For the covalent planar ($3d4s4p^2$ hybridization) Cu(II) complexes, for instance, the seventh electron has to be promoted from the 3*d* to 4*p* level differing from the configuration shown in Figure 4, in which the electron is only promoted from the non-bonding levels (d_{xy}, d_{yz}, and d_{zx}) to the antibonding level ($d_{x^2-y^2}$) (Kuroda and Ito 1955). Since

the promotion energy for the former is as high as 18 eV (Busch 1956) and much larger than that for the latter, 2 to 3 eV estimated from visible absorption spectra (Kuroda and Ito 1955), the latter type of electron configurations shown in the figures would be more reasonable energetically than the former one. The present scheme of electron configurations would serve to solve the objections raised by Nyholm (1953) to the hypothesis of electron promotion to a $4p$ level in Cu(II) complexes. Such a difference between an electron configuration based on the molecular orbital theory and that on the hybridized orbital theory comes from the fact that in the latter theory antibonding levels are neglected completely or assumed tacitly to be higher (more unstable) than a $4p$ or $5s$ level.

In the above treatment the intermixing of $3d$ orbitals with σ- or π-bonding orbitals of ligands are neglected just as in the so-called crystal field theory (see, for example, Jørgensen 1957). Since the intermixing does not change the symmetry of each level, its effect on the magnetic moment may be taken into account, in some degree, by changing the value of A. However, as shown in Figures 3, 7, and 9, the effective magnetic moments for the present cases are rather insensitive to the variation of A in the region of $x \approx 4$. Therefore, the introduction of the intermixing mentioned would not change the present results qualitatively.

As shown in Section II(a)–(e), the orbital contribution of electrons to the magnetic moment of Cu(II) complexes is expected only for tetrahedral, trigonal planar, and trigonal pyramidal configurations. Rây and Sen (1948) investigated the magnetic moments of a large number of tetra-coordinated Cu(II) complexes and concluded that the complexes having magnetic moments of 1·7 to 1·8 would have $3d4s4p^2$ planar structures and those having magnetic moments of 1·9 to 2·2 $4s4p^24d$ planar rather than $4s4p^3$ tetrahedral structures. According to the present theory, however, Cu(II) complexes of planar configurations must have magnetic moments of about 1·73, independent of which orbital $3d$ or $4d$ is used predominantly for bond formation, and those of tetrahedral configurations must have magnetic moments of about 2·2. Therefore, if two such distinct classes as suggested by Rây and Sen (1948) do exist, complexes with higher moments 1·9 to 2·2 should be expected to have tetrahedral rather than planar structures. Recently, Kishita, Muto, and Kubo have found that the effective magnetic moments of tri-coordinated Cu(II) complexes are smaller than the spin-only value 1·73. The magnetic moment of those complexes may be contributed not only from the spin magnetic moments but from the orbital motion of electrons also. However, the present theory predicts that the latter may increase instead of decrease the spin-only value for the magnetic moment. Therefore, the magnetic moments in those compounds may not be interpreted in terms of the orbital contribution. The interpretation given by Kishita, Muto, and Kubo that the compounds would be in dimeric form may be the more reasonable one at present.

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SOME STUDIES IN INORGANIC COMPLEXES

II. BISMUTH(III)

By G. J. SUTTON*

[*Manuscript received April 2, 1958*]

Summary

Complexes of bismuth halides and the ligand *o*-phenylenebisdimethylarsine have been prepared and studied. Conductivity and molecular weight determinations show that they are 5-covalent monomers of the type BiX_3.diarsine in which X is halogen. A study was also made of the 6-covalent complex Bi diarsine$_3$$(ClO_4)_3$. No coordination complex of phenanthroline was obtained, but some phenanthrolinium and dipyridylium salts of the type [phenan $H.H_2O$]$^+$[BiX_4]$^-$ and [dipy $H.H_2O$]$^+$[$BiCl_4$]$^-$ were investigated.

I. INTRODUCTION

The formation of unstable crystalline complexes of group 5 trihalides with dioxane has been described by Kelley and McCusker (1943). These are of the type $AsX_3.2D$, $SbX_3.2D$, and $BiCl_3.2D$ and are probably 5-covalent monomers, although they could be 6-covalent complexes by halogen bridging. It was considered that substitution of the unidentate dioxane as ligand by the more powerful chelating agent *o*-phenylenebisdimethylarsine might feasibly result in the formation of more stable complexes from which physical measurements could be made. In the present work, the reactions of tervalent bismuth with the diarsine as well as with the bases 1,10-phenanthroline and 2,2′-dipyridyl are described, whilst the results of similar investigations with antimony, arsenic, and phosphorus are treated in a subsequent paper.

The addition of the diarsine to solutions of bismuth chloride or bromide in dilute acid results in the formation of yellow chloro or bromo complexes corresponding to the formula BiX_3.diarsine. The iodo derivative is obtained as a bright red crystalline substance from tetraiodobismuthate ion by the addition of diarsine. These complexes are almost insoluble in cold water and are hydrolysed in hot water. They are very soluble in acetone and are sparingly soluble in ethanol or methanol. Conductivity measurements in nitrobenzene show that they are non-electrolytes, any slight conductance being due to traces of impurities or slight ionization of the complex. Molecular weight determinations in nitrobenzene and in acetone show that they are probably 5-covalent monomeric complexes like the halogen complexes $BiX_5^=$ (Ephraim and Masimann 1921; Gutbier and Muller 1932). However, it is possible that the 6*s* electrons of the bismuth atom are stereochemically active, making the complexes 6-covalent in the solid state. Since they are monomeric in nitrobenzene, it is unlikely that

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6-covalency is resorted to by halogen bridging, although they could be 6-covalent in acetone since this solvent is capable of occupying the sixth coordinating position. Tris(*o*-phenylenebisdimethylarsine)perchlorate was obtained as orange-yellow crystals by the addition of the diarsine to bismuth perchlorate in aqueous ethanol. It was found to be almost insoluble in common organic solvents except acetone, and detonated with considerable violence when heated. Since 5 mg of the salt shattered the combustion tube in a microanalysis, it was not possible to analyse this substance for carbon and hydrogen. However, other analytical data and its conductance as a terunivalent electrolyte in nitrobenzene show that it is a 6-covalent complex of bismuth. This was also confirmed by ionic weight determinations in nitrobenzene (cryoscopic) and in acetone (ebullioscopic). The orbitals used for bond hybridization in 5-covalent and 6-covalent complexes of bismuth and its congeners are a matter of conjecture. Since an octahedral structure would probably require the unpairing and promotion of the 6*s* electrons of the bismuth atom, the diarsine complex Bi diarsine$_3$(ClO_4)$_3$ and the corresponding complex of 1,10-phenanthroline Bi phenan$_3$(ClO_4)$_3$ described by Pfeiffer and Werdelmann (1950) are not necessarily octahedral.

In an attempt to form phenanthroline complexes of the bismuth halides, aqueous solutions of bismuth chloride or bromide were treated with sufficient acid to prevent hydrolysis and allowed to react with phenanthroline in ethanol. The colourless precipitates which formed were found to correspond to the formula BiX_4.phenan H_3O. If the reactions are allowed to proceed in acetone or ethanol without excess acid, mixtures of basic salts are obtained. The existence of the cation $Bi_4O_6^{4+}$ in less concentrated acid solutions has recently been established (Souchay and Peschanski 1948), and in any solvents capable of forming hydroxyl groups the formation of basic salts is likely. This would also be favoured by the addition of bases such as 1,10-phenanthroline or 2,2′-dipyridyl. The red iodo salt BiI_4.phenan H_3O was also obtained from the BiI_4^- ion by similar reaction with phenanthroline. Possible structures of these salts are (i) [phenan $H.H_2O$]$^+$[BiX_4]$^-$ and (ii) [H_3O]$^+$[phenan BiX_4]$^-$. In case (ii), the existence of the hydroxonium cation was considered as a possibility, since it occurs in the solid hydrates of perchloric and nitric acids. However, replacement of the cation by the triphenylmethylarsonium ion yielded the scarlet salt [Ph_3MeAs]$^+$[BiI_4]$^-$ with the iodo complex, although ion exchange was not effected with the chloro or bromo complexes, since these are almost insoluble in all common solvents and triphenylmethylarsonium chloride is not very soluble in organic solvents. Structure (i) was also supported by conductivity measurements in maximum concentration in nitrobenzene, the results being in agreement with those for other uniunivalent electrolytes. Ionic weight determinations were not possible for reasons of low solubility. Whilst the lone electron pair of one nitrogen atom of the base are used to coordinate the hydrogen ion, it is possible that hydrogen bonding in the water molecule is effected by the lone electron pair on the second nitrogen atom, thus giving rise to an aquophenanthrolinium cation. This is in agreement with the stability of the crystal lattices of the complexes to temperatures above 300 °C and is supported by the formation of 1,10-phenanthroline monohydrate from aqueous solution. The existence

of salts of the tetrahalidobismuthate anions has been well established by the use of the tetraiodobismuthate ion in alkaloid determinations as well as by the formation of such salts as the diazonium salt $[C_6H_5N{:}N]^+[BiCl_4]^-$ (Gilman and Gablunsky 1941). The dipyridylium salt (dipy $H.H_2O$][$BiCl_4$] was also obtained

TABLE 1

MOLECULAR CONDUCTIVITIES, MOLECULAR AND IONIC WEIGHTS OF BISMUTH COMPOUNDS

D, *o*-phenylenebisdimethylarsine; phen, 1,10-phenanthroline; dipy, 2,2′-dipyridyl; *M*, molecular; nb, nitrobenzene (cryoscopic method); ac, acetone (ebullioscopic method); conc., concentration; mhos, reciprocal ohms

Substance	*M* Conductivity		*M* or Ionic Weight			
	mhos	*M* Conc.	Found	Calc.	Conc. (%)	Solvent
$BiCl_3$.D	0·69	0·0049	630	602	0·29	nb
	0·80	0·0040	580	602	0·24	nb
	0·60	0·0044	585	602	0·52	ac
	1·20	0·0039	598	602	0·62	ac
$BiBr_3$.D	0·53	0·0030	680	735	0·84	nb
	0·66	0·0025	690	735	0·22	nb
	0·77	0·0024	690	735	0·58	ac
	0·62	0·0029	710	735	0·63	ac
BiI_3.D	0·51	0·0056	830	876	0·49	nb
	0·62	0·0026	855	876	0·66	nb
	0·48	0·0029	855	876	0·49	ac
			857	876	0·68	ac
$BiD_3(ClO_4)_3$	53·3	0·0015	316	341	0·88	nb
	53·5	0·0005	328	341	0·26	ac
			317	341	0·26	ac
[phen H_2O][$BiCl_4$]	20·1	0·0004				
[phen H_2O][$BiBr_4$]	19·7	0·0003				
[phen H_2O][BiI_4]	25·2	0·0031				
[dipy H_2O][$BiCl_4$]	24·5	0·0004				
[Ph_3MeAs][BiI_4]	20·1	0·0038	440	519	0·47	ac
	19·9	0·0031				

by using 2,2′-dipyridyl instead of 1,10-phenanthroline, the method of preparation and properties being similar to those of the corresponding phenanthrolinium salt.

The conductivity and ionic weight determinations are summarized in Table 1 and in some cases include results from additional preparations. In all cases the conductivity measurements were carried out in nitrobenzene.

II. Experimental

The molecular conductivity measurements were determined in pure nitrobenzene at 25 °C using a conductivity-measuring bridge Philoscope model GM4249/01 and cell GM4221. The purifications of the nitrobenzene and the acetone used in the physical measurements have been described in Part I of this series (Sutton 1958).

(*a*) *Trichloromono*(o-*phenylenebisdimethylarsine*) *Bismuth*.—Bismuth nitrate pentahydrate (1 mM) was dissolved in 2N hydrochloric acid (50 ml) and the diarsine (1 mM) added in ethanol (5 ml) with stirring. The pale yellow precipitate which formed was filtered, washed with water, ethanol, and ether (each 2 ml), recrystallized from acetone, and dried over sulphuric acid in a vacuum desiccator. The comparatively low yield (0·32 g) was attributable to rejecting the supernatant liquid after the first crystallization. The pale lemon-yellow cubes which resulted were found to melt with decomposition at 227 °C (Found: C, 20·1; H, 2·9; Cl, 17·6; Bi, 34·5%. Calc. for $C_{10}H_{16}As_2Cl_3Bi$: C, 20·0; H, 2·7; Cl, 17·6; Bi, 34·8%).

(*b*) *Tribromomono*(o-*phenylenebisdimethylarsine*) *Bismuth*.—The latter procedure was repeated using hydrobromic acid in lieu of hydrochloric acid, when yellow crystals (0·45 g), which melted at 224 °C, were obtained (Found: C, 16·5; H, 2·1; Br, 32·4%. Calc. for $C_{10}H_{16}As_2Br_3Bi$: C, 16·3; H, 2·2; Br, 32·7%).

(*c*) *Tri-iodomono*(o-*phenylenebisdimethylarsine*) *Bismuth*.—Bismuth nitrate pentahydrate (1 mM) was dissolved in the smallest quantity of 2N hydrochloric acid and the solution treated with sufficient 0·5M potassium iodide solution to redissolve the brown bismuth iodide which formed. The orange-red solution was treated with diarsine (1 mM) in ethanol (5 ml) with constant stirring. The scarlet precipitate which formed was washed with small quantities of water, ethanol, and ether and recrystallized from acetone (yield 0·60 g). The red crystals decomposed at 205 °C (Found: C, 13·9; H, 1·8; I, 43·3%. Calc. for $C_{10}H_{16}As_2I_3Bi$: C, 13·7; H, 1·8; I, 43·5%).

(*d*) *Tris*(o-*phenylenebisdimethylarsine*) *Bismuth*(*III*) *Perchlorate*.—Basic bismuth carbonate (0·5 mM) was dissolved in 70% perchloric acid (8 ml) with heating, centrifuged, and cooled. Diarsine (3 mM) in ethanol (45 ml) was added cautiously and the mixture stirred steadily. An orange colour developed in the solution and bright canary-yellow crystals settled out. The latter were separated by centrifugation, washed once with ethanol (5 ml), twice with ether (5 ml), and dried in a vacuum desiccator over concentrated sulphuric acid (yield 0·36 g). The substance decomposed with violence at about 200 °C and it was not possible to carry out carbon and hydrogen determinations (Found: Cl, 7·5; Bi, 15·1%. Calc. for $C_{30}H_{48}As_6O_{12}Cl_3Bi$: Cl, 7·8; Bi, 15·3%).

(*e*) *Phenanthrolinium Tetrachlorobismuthate*(*III*) *Monohydrate*.—Bismuth nitrate pentahydrate (1 mM) was dissolved in the smallest quantity of 2N nitric acid and conc. hydrochloric acid (3 ml) added. Ethanol (6 ml) was then added followed by 1,10-phenanthroline monohydrate (1 mM) in ethanol (3 ml) with stirring. The fine white microcrystalline prisms which formed were separated by centrifugation, washed with successive small portions of ethanol and then with ether, dried in an oven at 100 °C, and then in a vacuum desiccator over conc. sulphuric acid (yield 0·53 g). The salt, which decomposed at 316 °C, was found to be almost insoluble in common organic solvents, but was sufficiently soluble in nitrobenzene for physical measurements to be made (Found: C, 26·4, 26·4; H, 1·9, 1·7; N, 4·6; Cl, 25·7%. Calc. for $C_{12}H_{11}N_2OCl_4Bi$: C, 26·2; H, 2·0; N, 4·9; Cl, 25·7%).

(*f*) *Phenanthrolinium Tetrabromobismuthate*(*III*) *Monohydrate*.—Using conc. hydrobromic acid (5 ml) in place of hydrochloric acid in the above preparation and repeating the aforementioned procedure, the bromo complex was obtained as a pale yellow microcrystalline powder (yield 0·70 g). The salt decomposed at 310 °C (Found: C, 20·2, 20·1; H, 1·6, 1·6; N, 3·4;* Br, 43·5%. Calc. for $C_{12}H_{11}N_2OBr_4Bi$: C, 19·8; H, 1·5; N, 3·8; Br, 43·9%).

(*g*) *Phenanthrolinium Tetraiodobismuthate*(*III*) *Monohydrate*.—The aforementioned procedure was repeated using sufficient hydriodic acid to effect solution of the brown bismuth iodide which

* It is not unusual for heterocyclics to give low nitrogen figures on analysis.

first formed, prior to the addition of the phenanthroline (1 mM) in ethanol. The orange-red microcrystalline powder which resulted (0·88 g) was found to decompose at 305 °C (Found: C, 15·5; H, 1·3; N, 2·8; I, 55·0%. Calc. for $C_{12}H_{11}N_2OI_4Bi$: C, 15·7; H, 1·2; N, 3·1; I, 55·4%).

(*h*) *Dipyridylium Tetrachlorobismuthate(III) Monohydrate.*—The procedure adopted was the same as that for the corresponding phenanthroline complex, using 2,2′-dipyridyl (1 mM) in lieu of 1,10-phenanthroline. The white silky precipitate which formed was found to melt at 252 °C (decomp.) (yield 0·50 g) (Found: C, 22·5; H, 1·8; Cl, 27·1%. Calc. for $C_{10}H_{11}N_2OCl_4Bi$: C, 22·8; H, 2·1; Cl, 26·9%).

(*i*) *Triphenylmethylarsonium Tetraiodobismuthate(III).* — Phenanthrolinium tetraiodobismuthate(III) monohydrate was dissolved in the smallest quantity of a solution consisting of equal volumes of acetone, water, and ethanol. A saturated solution of triphenylmethylarsonium chloride in water was added in twofold excess with rapid stirring. The bright red precipitate which formed slowly was washed with water to remove traces of chloride, and equal parts of ethanol and acetone to remove any of the original complex, and dried in a vacuum desiccator over conc. sulphuric acid (Found: C, 22·3; H, 1·7; I, 48·5%. Calc. for $C_{19}H_{18}AsI_4Bi$: C, 22·0; H, 1·8; I, 48·9%).

Halogens were determined gravimetrically as silver halide and bismuth gravimetrically as oxide.

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SOME STUDIES IN INORGANIC COMPLEXES

III. ANTIMONY(III), ARSENIC(III), AND PHOSPHORUS(III)

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Summary

A study has been made of complexes of the halides of antimony, arsenic, and phosphorus with the chelating ligand *o*-phenylenebisdimethylarsine. Conductivity and molecular weight determinations in nitrobenzene show that these are probably 5-covalent monomers of the type $SbX_3.D$, AsX_3D, and $PX_3.D$, in which X is halogen and D is diarsine. However, in this solvent there is a progressive tendency towards ionization from Sb to P and from Cl to I, so that the iodo complexes of arsenic and phosphorus are partly ionized as $[AsI_2D]^+I^-$ and $[PI_2D]^+I^-$ respectively. This is also in accordance with the preparation of the perchlorate $[AsI_2D]^+[ClO_4]^-.H_2O$ from the complex $[AsI_2D]^+I^-$. A study was also made of the phenanthrolinium salts $[phenanH.H_2O]^+[SbX_4]^-$, although no compounds were obtained in which the base is coordinated to the metal.

I. INTRODUCTION

The formation of complexes of the bismuth halides of the type $BiX_3.D$† with *o*-phenylenebisdimethylarsine prompted this investigation with the progressively less basic congeners antimony, arsenic, and phosphorus. The possibility of reactivity of the base 1,10-phenanthroline towards antimony was also considered, following the recent study of a 4-covalent trichloromonopyridine antimony complex by Das and Pami (1956). The antimony halides react with *o*-phenylenebisdimethylarsine in ethanol to form microcrystalline precipitates of the type $SbX_3.D$. The complexes are chloride (very pale pink), bromide (very pale green), and iodide (yellow) respectively, and they are insoluble in solvents of low dielectric constant with the exception of dioxane in which hydrolysis takes place. They are also hydrolysed, at temperatures above 40 °C, in other solvents capable of forming hydroxyl groups by resonance, as well as by methanol, ethanol, acetone, and water. However, they were found to be sufficiently soluble in nitrobenzene for molecular conductivities and molecular weight determinations to be made. Hydrolysis is so rapid at room temperatures in ethanol and acetone that it is necessary to prepare the corresponding diarsine derivatives of the arsenic and phosphorus halides in solvents such as carbon tetrachloride or in carbon disulphide. From carbon tetrachloride solution, the following substances were precipitated as fine powdery solids : $AsCl_3.D$ (white), $AsBr_3.D$ (pale yellow), $AsI_3.D$ (yellow), $PBr_3.D$ (white), and $PI_3.D$ (yellow). In attempts to form the diarsine complex $[PCl_4.D]^+[PCl_6]^-$, " phosphorus pentachloride " was allowed

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† In the present paper D is used for *o*-phenylenebisdimethylarsine and X for halogen.

to react with the diarsine in carbon tetrachloride. However, reduction to the complex PCl_3.D took place in each case, the products being contaminated with adsorbed oxidation products of the diarsine. Repetitive conductance and molecular weight determinations in nitrobenzene on different samples of the antimony, arsenic, and phosphorus complexes of the diarsine showed that most of the complexes may be described as 5-covalent monomers. However, it was noticed that whilst there was a slight increase in conductivity from antimony to phosphorus and from chlorine to iodine in the complexes investigated, this difference was sufficiently great in the case of the iodo complexes of arsenic and phosphorus to indicate that considerable dissociation takes place in nitrobenzene. Knowledge of the degree of ionic character in the solid state would require X-ray investigations. The ionic weights in nitrobenzene and the formation of the perchlorate $[AsI_2.D]^+[ClO_4]^-.H_2O$ from the arsenic complex show that the ionization takes place by the splitting off of an iodide ion as in $[AsI_2.D]^+I^-$ and $[PI_2D]^+I^-$ and not by the formation of the dimers $[AsI_2D_2]^+[AsI_4]^-$ and $[PI_2D_2]^+[PI_4]^-$. In order to prepare the perchlorate $[AsI_2D]^+[ClO_4]^-.H_2O$ it was necessary to treat a cold solution of the original iodo complex in acetone with 70 per cent. perchloric acid. Since decomposition, due to water, is almost instantaneous in this solvent in the case of the phosphorus complex the perchlorate was not obtainable. Ion exchange using silver perchlorate in chloroform was impracticable owing to the precipitation of silver iodide. Since the degree of ionization is small in the case of the other diarsine complexes investigated, no other corresponding perchlorates were obtained apart from a trace of white crystalline material from the complex $AsBr_3$.D using a large excess of 70 per cent. perchloric acid.

From the work of Byström (1951) it may be inferred that in the ion SbF_5^- the paired 5*s*-electrons of the antimony atom are stereochemically active, thus giving rise to an octahedral structure. However, in the diarsine complexes of bismuth, antimony, and their congeners it is more likely that the paired *s*-electrons are partly fed back into the $d\pi$-orbitals of the arsenic atom, thus reinforcing the σ-bond by a certain degree of π-bonding. This supposition is fortified by the decrease in reactivity of 1,10-phenanthroline towards the members of Group 5B where the conditions for π-bonding are less in the case of the nitrogen atom and can only be accomplished by resonance in the heterocyclic ring. Furthermore, both indium and thallium in Group 3B are readily coordinated by phenanthroline but have very low reactivity towards the diarsine. With these metals the conditions for π-bonding are considerably lessened, since there are no corresponding paired *s*-electrons available in the oxidation state M^{3+}. The members of Group 3B, being more basic than those of Group 5B, should be more reactive towards the more negative nitrogen atom than towards arsenic, whilst the 5B members should react more readily with the less negative arsenic atom. However, the supposition that the diarsine complexes of antimony and its congeners are 5-covalent could account for their tendency to decompose in solvents capable of forming hydroxyl groups, when solvent molecules can occupy the sixth coordinating position ; compared with their greater solution stability in solvents where this is less likely. It is also noteworthy that with rise in atomic number

the lone pair of *s*-electrons are more effectively shielded from the positive nucleus of the atom, so that the restraint on them is less and they become more readily available for π-bonding; hence the bismuth complexes of the diarsine are the most solution-stable of those of Group 5B.

TABLE 1

MELTING POINTS, MOLECULAR CONDUCTIVITIES, AND MOLECULAR WEIGHTS OF ANTIMONY, ARSENIC, AND PHOSPHORUS COMPOUNDS

Substance	M.P. (°C)	Molecular Conductivity 25 °C		Molecular Weight		
		mhos	M Conc.	Found	Calc.	Conc. (%)
$SbCl_3$.D	218	0·58	0·0035	470	514	0·86
		0·41	0·0047	485	514	0·72
$SbBr_3$.D	222	1·08	0·0030	604	648	0·64
		1·00	0·0061	645	648	0·60
SbI_3.D	210	3·84	0·0026	670	789	0·95
		3·96	0·0032	653	789	0·46
$AsCl_3$.D	205d	1·02	0·0056	437	467	0·80
$AsBr_3$.D	230d	1·87	0·0028	555	601	0·74
		2·04	0·0023	548	601	0·95
AsI_3.D	160d	10·40	0·0018	554	742	0·83
		10·40	0·0023			
		10·50	0·0015			
PBr_3.D	215d	2·25	0·0060	400	423	0·50
PI_3.D	132d	17·9	0·0030	368	698	0·80
		17·8	0·0034	340	698	0·67
$[AsI_2D][ClO_4].H_2O$ ..	195	25·0	0·0029	324	733	0·25
$[PhenH.H_2O][SbCl_4]$ ..	190	19·6	0·0038			
$[PhenH.H_2O][SbBr_4]$	218	19·4	0·0020			
$[PhenH.H_2O][SbI_4]$ ..	230	19·3	0·0017			

From solutions of antimony halides in ethanol, having sufficient excess halide acid to prevent hydrolysis, 1,10-phenanthroline reacts to produce insoluble phenanthrolinium salts of the type $[PhenanH.H_2O]^+[SbX_4]^-$, similar to those of bismuth. The chloro and bromo complexes are white, whilst the iodo complex is red. Their structure as uniunivalent electrolytes was verified by conductance measurements in nitrobenzene. It is likely that the water molecule is attached

by hydrogen bonding using the lone electron pair of the available nitrogen atom of the base since the salts are stable to at least 190 °C. Ionic weight measurements were indeterminable for reasons of low solubilities in suitable solvents.

The melting points, molecular conductivities, and molecular weights of the compounds described in this work are summarized in Table 1, all physical measurements having been carried out in A.R. nitrobenzene.

II. Experimental

The conductivity measurements and methods of solvent purification were carried out in the same manner as described in previous papers.

(*a*) *Trichloromono(o-phenylenebisdimethylarsine)antimony*

Antimony trichloride (1 mM) in ethanol (25 ml) was treated with sufficient hydrochloric acid to prevent hydrolysis and *o*-phenylenebisdimethylarsine (1 mM) in ethanol (5 ml) added with stirring. A pink colour developed and on standing pale pink crystals settled out. These were washed with successive small portions of ethanol and ether and dried in a vacuum desiccator over concentrated sulphuric acid (yield 0·32 g) (Found: C, 23·3; H, 3·0; Cl, 21·1%. Calc. for $C_{10}H_{16}As_2Cl_3Sb$: C, 23·4; H, 3·1; Cl, 20·8%).

(*b*) *Tribromomono(o-phenylenebisdimethylarsine)antimony*

The aforementioned procedure was repeated using an excess of concentrated hydrobromic acid in place of hydrochloric acid. On the addition of diarsine (1 mM) a pale green colour developed and pale green crystalline laminae settled out which were washed and dried as before (yield 0·38 g) (Found: C, 18·7; H, 2·6; Br, 37·0%. Calc. for $C_{10}H_{16}As_2Br_3Sb$: C, 18·6; H, 2·5; Br, 37·1%).

(*c*) *Tri-iodomono(o-phenylenebisdimethylarsine)antimony*

The above procedure was carried out using a slight excess of hydriodic acid instead of hydrochloric acid. On the addition of diarsine (1 mM) to the solution, a yellow precipitate was formed which was washed free of impurities and dried as before (yield 0·61 g) (Found: C, 15·1; H, 1·9; I, 48·8%. Calc. for $C_{10}H_{16}As_2I_3Sb$: C, 15·2; H, 2·1; I, 48·4%).

(*d*) *Trichloromono(o-phenylenebisdimethylarsine)arsenic*

Anhydrous arsenious chloride (1 mM) was dissolved in sufficient A.R. carbon tetrachloride and after centrifuging treated with diarsine (1 mM) in carbon tetrachloride (5 ml). The white precipitate which formed was allowed to settle and was separated by centrifuging. It was washed several times with carbon tetrachloride and then with ether and dried in a vacuum desiccator (yield 0·37 g) (Found: C, 25·5; H, 3·5; Cl, 22·5%. Calc. for $C_{10}H_{16}As_3Cl_3$: C, 25·7; H, 3·5; Cl, 22·8%).

(*e*) *Tribromomono(o-phenylenebisdimethylarsine)arsenic*

Anhydrous arsenious bromide (1 mM) was allowed to react with the diarsine (1 mM) according to the above procedure and the pale yellow crystalline precipitate which formed was washed and dried as before (yield 0·46 g) (Found: C, 19·9; H, 3·0; Br, 40·0%. Calc. for $C_{10}H_{16}As_3Br_3$: C, 20·0; H, 2·7; Br, 39·8%).

(*f*) *Mono(o-phenylenebisdimethylarsine)arsenic(III) Iodide*

The aforementioned procedure was repeated using arsenious iodide (1 mM). The bright yellow precipitate which formed was washed free from impurities, using carbon tetrachloride and small quantities of diethyl ether, and dried in a vacuum desiccator (yield 0·61 g) (Found: C, 16·4; H, 2·4; I, 5·0%. Calc. for $C_{10}H_{16}As_3I_3$: C, 16·2; H, 2·2; I, 5·5%). A second preparation yielded 0·67 g.

(*g*) *Di-iodomono*(o-*phenylenebisdimethylarsine*)*arsenic*(*III*) *Perchlorate Monohydrate*

The complex AsI_3.D (0·5 g) was dissolved in the smallest quantity of acetone at 30 °C, filtered, and treated with 70% perchloric acid (4 ml). On stirring, a pale yellow crystalline precipitate settled out. This was immediately separated by centrifuging, washed several times with small quantities of acetone, and dried in a vacuum desiccator over sulphuric acid (yield 0·4 g) (Found: C, 16·4; H, 2·7%. Calc. for $C_{10}H_{18}As_3I_2ClO_5$: C, 16·4; H, 2·5%).

(*h*) *Tribromomono*(o-*phenylenebisdimethylarsine*)*phosphorus*

Phosphorus tribromide (1 mM) was allowed to react with diarsine (1 mM) in A.R. carbon tetrachloride with constant stirring. The white flaky precipitate which formed was washed with small quantities of carbon tetrachloride and diethyl ether after separation by centrifuging (yield 0·36 g) (Found: C, 21·9; H, 3·0; Br, 43·0%. Calc. for $C_{10}H_{16}As_2PBr_3$: C, 21·6; H, 2·9; Br, 43·0%).

(*i*) *Mono*(o-*phenylenebisdimethylarsine*)*phosphorus*(*III*) *Iodide*

The latter procedure was repeated using phosphorus tri-iodide (1 mM) in place of phosphorus tribromide. A yellow precipitate was formed (yield 0·42 g). The substance was found to be crystallizable from anhydrous diethyl ether (Found: C, 17·2; H, 2·4; I, 54·0%. Calc. for $C_{10}H_{16}As_2PI_3$: C, 17·2; H, 2·3; I, 54·5%).

(*j*) *Reaction of Phosphorus Pentachloride with* o-*Phenylenebisdimethylarsine*

Phosphorus pentachloride (2 mM as monomer) was dissolved in sufficient A.R. carbon tetrachloride to form a saturated solution and diarsine (1 mM) in carbon tetrachloride (4 ml) added with stirring. An opalescence developed and after standing for 20 min a silky white precipitate settled out. This was separated by centrifuging and washed several times with carbon tetrachloride (yield 0·31 g). Repeated crystallization from diethyl ether failed to give a pure substance as PCl_3.D, the substance being contaminated with some organic product of oxidation of the diarsine (Found: C, 30·4, 29·8, 29·2; H, 4·4, 4·5, 3·9%. Calc. for $C_{10}H_{16}As_2PCl_3$: C, 28·4; H, 3·8%).

(*k*) *Phenanthrolinium Tetrachloroantimonate*(*III*) *Monohydrate*

Antimony trichloride (1 mM) in ethanol (15 ml) was treated with drops of 10N hydrochloric acid to redissolve any basic salt, and 1,10-phenanthroline (1 mM) in ethanol (5 ml) added with stirring. The fine white crystalline precipitate which formed was washed repeatedly with ethanol and ether after separation by centrifuging and dried over concentrated sulphuric acid in a vacuum desiccator (yield 0·49 g) (Found: C, 31·0; H, 2·7; N, 5·5; Cl, 31·0%. Calc. for $C_{12}H_{11}N_2OCl_4Sb$: C, 31·1; H, 2·4; N, 6·1; Cl, 30·7%).

(*l*) *Phenanthrolinium Tetrabromoantimonate*(*III*) *Monohydrate*

The above procedure was repeated using antimony tribromide (1 mM) in ethanol together with sufficient hydrobromic acid to offset hydrolysis. The experimental procedure followed that for the chloro complex. The product was a white microcrystalline powder (yield 0·67 g) (Found: C, 22·5, 22·5, 22·7; H, 1·8, 1·7, 1·7; Br, 49·4%. Calc. for $C_{12}H_{11}N_2OBr_4Sb$: C, 22·5; H, 1·7; Br, 49·8%).

(*m*) *Phenanthrolinium Tetraiodoantimonate*(*III*) *Monohydrate*

The above procedure was repeated using antimony chloride (1 mM) in ethanol (15 ml) and concentrated hydriodic acid (5 ml). On the addition of the phenanthroline (1 mM) in ethanol (5 ml) an orange microcrystalline precipitate was formed which was separated by centrifuging, washed with ethanol and ether, and dried over sulphuric acid in a vacuum desiccator (yield 0·81 g) (Found: C, 17·6; H, 1·5; N, 3·1; I, 60·8%. Calc. for $C_{12}H_{11}N_2OI_4Sb$: C, 17·4; H, 1·6; N, 3·4; I, 61·3%).

III. Acknowledgment

The author is grateful to Dr. E. Challen of the Microanalytical Laboratory for some of the carbon and hydrogen analyses.

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THE RESOLUTION OF [TRIS{*CIS*-DIHYDROXYBISETHYLENE‡ DIAMINECOBALT(III)}COBALT(III)] NITRATE

By H. A. Goodwin,* E. C. Gyarfas,† and D. P. Mellor‡

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Summary

The resolution of [tris{*cis*-dihydroxybisethylenediaminecobalt(III)}cobalt(III)] nitrate (hexol nitrate) into four of the eight theoretically possible optical isomers using potassium *d*- and *l*-antimonyl tartrate is described. The reactions involved in the formation of the optically active isomers of the hexol ion show less stereospecificity than those of similar complexes studied by earlier investigators.

I. Introduction

The complex, [tris{*cis*-dihydroxybisethylenediaminecobalt(III)}cobalt(III)] nitrate (hexol nitrate) was first prepared by Werner (1907) who, on the basis of its composition and chemical reactions, proposed for it a structure analogous to the one he had assigned to the corresponding ammonia compound, namely, [tris{*cis*-dihydroxytetramminecobalt(III)}cobalt(III)] nitrate (hexol nitrate A), $[Co\{Co(NH_3)_4(OH)_2\}_3](NO_3)_6$. He later confirmed the structure of hexol nitrate A by resolving it into its optical enantiomers (Werner 1914). This communication describes the resolution of hexol nitrate.

The ligands $\{Co(en)_2(OH)_2\}^+$ which surround the central cobalt atom in the hexol ion can exist in two optically active forms. Thus for the complex as a whole eight optical forms are theoretically possible. If D and L denote the configuration of the complex as a whole, and *d* and *l* the configuration of the ligands then the eight forms would be:

D *ddd*	L *lll*
D *ddl*	L *lld*
D *dll*	L *ldd*
D *lll*	L *ddd*

Other investigators who have studied systems of this kind have isolated only two of the eight possible isomers. Jaeger and Blumendal (1928) in a study of the tris *trans*-1,2-diamino*cyclo*pentane complexes of cobalt(III) and rhodium(III) succeeded in isolating in each instance only two isomers which were presumed to be L *ddd* and D *lll* forms. Lifschitz (1925) was able to isolate the two forms, D *ddd* and L *ddd*, of the more soluble geometric isomer of tris-*d*-alaninecobalt(III).

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In the present work, two mirror-image pairs, designated $D_I L_I$ and $D_{II} L_{II}$, have been isolated. The resolutions were effected by means of potassium *d*- and *l*-antimonyl tartrate. The resolving anions were removed by precipitating the optically active complex ions as thiocyanates. From the diastereoisomers formed by treating hexol nitrate with *d*-antimonyl tartrate the D_I and L_{II} isomers were obtained. A similar process in which the *l*-antimonyl tartrate was used yielded the D_{II} and L_I isomers. The results not only confirm the structure put forward by Werner but also show that in this complex the configuration of the ligand has a less marked tendency to influence the configuration of the complex as a whole than might have been expected from the work of earlier investigators. In other words, the stereospecificity displayed in the formation of optical isomers of the hexol ion is by no means absolute. It is uncertain whether both *d*- and *l*-forms of the ligand are present in the one molecule of hexol nitrate since the two pairs could be D *lll* L *ddd* and D *ddd* L *lll*. It has not been possible to obtain any evidence on this point.

Although the specific rotations of the two pairs were quite close:

$$[\alpha]_D = \pm 3920^\circ \text{ for the } D_I L_I \text{ pair,}$$
$$[\alpha]_D = \pm 3620^\circ \text{ for the } D_{II} L_{II} \text{ pair,}$$

the rates of "racemization"* in aqueous solution were conspicuously different.

The rates of racemization which followed first-order reaction kinetics were:

$$k_{40\,^\circ C} = 0{\cdot}11 \times 10^{-3} \text{ sec}^{-1} \text{ for the } D_I L_I \text{ pair,}$$
$$k_{40\,^\circ C} = 0{\cdot}11 \times 10^{-4} \text{ sec}^{-1} \text{ for the } D_{II} L_{II} \text{ pair.}$$

From the nature of the methods used in their preparation, the difference in specific rotations, and in rates of racemization, it is evident that there are two distinct mirror-image pairs of isomers.

The active forms lost their rotations quite quickly in the presence of hydrochloric acid; in strongly alkaline solution their rotation vanished almost instantaneously. Loss of activity in these circumstances was in all probability due to the formation of inactive dichloro-, chloroaquo-, diaquo-, aquohydroxy-, or dihydroxybisethylenediamine complexes.

Thus, when converting the diastereoisomers formed with antimonyl tartrate to the thiocyanate, it was essential to use a weak base such as sodium acetate to dissolve them. The antimonyl tartrates were so insoluble in water that, once dissolved in saturated sodium acetate solution, they were immediately reprecipitated if the solution was even slightly diluted.

To obtain the antimonyl tartrates in crystalline form, it was found essential to have a reasonably dilute solution of hexol at 40 °C and to add antimonyl tartrate, drop by drop at first and then slowly with much scratching of the sides of the vessel. Unless this procedure was followed an intractable tar was formed.

* The question whether this is a true racemization is discussed in a later section. Although there is considerable doubt on this point, the term racemization will be used throughout in order to avoid circumlocution.

In an attempt to obtain at least one DL pair from the same solution of hexol nitrate using only one form of antimonyl tartrate as the resolving agent, the whole of the nitrate was fractionally precipitated by adding the *d*-antimonyl tartrate in portions. It was found that the rotations of successive fractions changed direction often and quite abruptly. In fact, the more fractions obtained, the more often the rotation changed direction. In a series in which 10 fractions were obtained, the rotations of the fractions in order of precipitation were:

(1) +2·95 (2) +2·53 (3) +0·17 (4) −1·88 (5) +0·50
(6) −2·26 (7) +0·44 (8) −0·95 (9) +0·42 (10) −0·19.

In order to test the hypothesis that the peaks in the rotations were due to the existence of the whole eight possible isomers, a large quantity of hexol nitrate (35 g) was treated to yield 32 fractions. The results are presented in Table 1.

TABLE 1

SPECIFIC ROTATION OF 32 FRACTIONS OF HEXOL *d*-ANTIMONYL TARTRATE

Rotations are for a 0·1 per cent. solution, measured in the sodium D line

Fraction	Rotation	Fraction	Rotation	Fraction	Rotation
1	+3·10°	12	−1·46°	23	+0·90°
2	+3·10°	13	−1·70°	24	−1·30°
3	+2·90°	14	−1·33°	25	−1·06°
4	+3·30°	15	−0·30°	26	−0·53°
5	+3·29°	16	−1·56°	27	−0·53°
6	+2·82°	17	−1·90°	28	−0·44°
7	+2·80°	18	+0·45°	29	−0·70°
8	+2·70°	19	−1·90°	30	+0·98°
9	+2·60°	20	+0·30°	31	+0·20°
10	+1·70°	21	−1·60°	32	+0·20°
11	−0·45°	22	−1·80°		

A plot of the specific rotation [α] against the number of fractions for this fractionation revealed that the rotation changed direction no less than 13 times (see Fig. 1). From this result, it is evident that each peak does not represent one of the eight isomers theoretically possible. Some other explanation must be found for this anomalous behaviour. One possibility is that it arises from the racemization of the antipode of a form precipitated earlier in the process. The time taken to isolate the 32 fractions was greater than the half-life for racemization of the form first precipitated. It took 5 hr to precipitate the 32 fractions, whereas the half-life of racemization was about 3 hr. It is a moot point whether the disappearance of rotation is indeed a true racemization. Racemization of the form D *ddd* would involve such steps as (i) dissociation of the *d*-ligands, (ii) racemization of the *d*-ligands, (iii) recombination of the *d*- and *l*-ligands to form L *lll* D *lll* D *ddd* L *ddd*. If the disappearance of optical rotation is a true racemization, it must be a very complex process.

The loss of rotation could be due to decomposition of the hexol ion. There is certainly evidence of this in solutions of hexol thiocyanate that have been

allowed to stand at room temperature for a few days. In these there is a marked colour change from brown to red. All attempts to obtain active diastereoisomers from the racemized thiocyanates failed. This would seem to indicate that true racemization does not take place. Neither of these possible mechanisms for the disappearance of rotation affords a satisfactory explanation of the anomalous behaviour of the rotation during fractionation.

The rates of racemization of the thiocyanates derived from several of the fractions were determined in order to see whether some at least of the changes in direction of rotation were due to the presence of more than one DL-pair. The two thiocyanates that differed most conspicuously were those derived from the first and fourth in the series of 10 fractions set out above. The fourth fraction was the first that was strongly *laevo*.

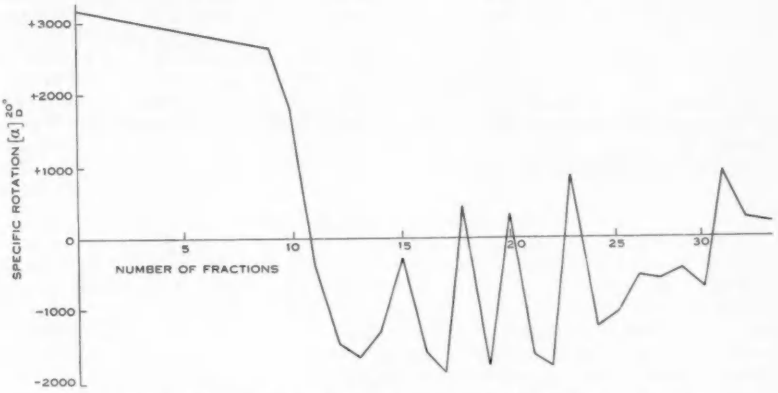

Fig. 1.—Fractionation of hexol (35 g) with *d*-antimonyl tartrate.

In the second, more elaborate fractionation using *d*-antimonyl tartrate (Table 1), it was found that the thiocyanates derived from the first strongly *dextro* and the first strongly *laevo* differed in the rates of "racemization" by a factor of 10. These two fractions, then, were considered not to be mirror images. To obtain mirror images of these two forms, potassium *l*-antimonyl tartrate was used as the resolving agent.

All attempts to determine the configuration of the ligands in the two pairs ($D_I L_I$ and $D_{II} L_{II}$) by detaching them from the central cobalt atom as Werner did, failed. No activity could be detected in any of the ligands so detached. This characteristic of the hexol ion renders it unsuitable for a thorough investigation of stereospecificity in metal complexes and further work on it was therefore abandoned.

II. Experimental

(*a*) *Potassium* l-*Antimonyl Tartrate*

In order to obtain *l*-tartaric acid, *d*-tartaric acid was racemized by the method of Campbell, Slotin, and Johnson (1933). The racemic acid resolved by the method of Marckwald (1896) and *l*-tartrate was isolated as potassium hydrogen tartrate.

Potassium *l*-hydrogen tartrate (5 g) was then thoroughly mixed with antimonious oxide (3·75 g) and the mixture ground to a fine paste with water. The paste was then digested on the water-bath for ½ hr. Water (10 ml) was then added and the mixture boiled. The hot solution was filtered and potassium *l*-antimonyl tartrate crystallized from the filtrate on cooling. Yield 6 g.

(*b*) *Racemic Hexol Nitrate*

This was prepared by the method of Werner (1907). Cobalt nitrate (145 g) was dissolved in water (150 ml) and a 10% solution of ethylenediamine (300 ml) was slowly added. The mixture was stirred vigorously until a red-brown colour developed. The small amount of cobalt oxide which deposited was filtered and the filtrate poured into a large evaporating basin. The product slowly crystallized and was collected after 2 days. It was washed with a little water and air-dried.

(*c*) D$_I$-*Hexol* d-*Antimonyl Tartrate Octadecahydrate*

D$_I$-Hexol (10 g) was dissolved in water (400 ml) and the solution warmed to 40 °C. To this was slowly added a near-boiling solution of potassium *d*-antimonyl tartrate (4 g) in water (25 ml) with continual scratching of the sides of the vessel. A voluminous pink-brown crystalline precipitate of the diastereoisomer deposited. This was washed with water, ethanol, and ether and air-dried. A convenient method for determining the specific rotation* of this, as well as the other diastereoisomers, was to grind a small amount with an excess of sodium acetate, add water, filter off the precipitated Sb_2O_3, and estimate the concentration of hexol colorimetrically. A 0·1% aqueous solution gave $[\alpha]_D$ +3·20° (Found: C, 15·7; H, 3·9; N, 6·1%. Calc. for $[Co_4(C_2N_2H_8)_6(OH)_6](C_4H_4O_7Sb)_6.18H_2O$: C, 15·8; H, 4·2; N, 6·1%).

(*d*) D$_I$-*Hexol Thiocyanate Monohydrate*

D$_I$-Hexol *d*-antimonyl tartrate was ground with an excess of sodium acetate and water (3 ml/g of diastereoisomer) added. The mixture was then filtered with the aid of fine pulp into a dry vessel and solid ammonium thiocyanate was added to the filtrate. On scratching the sides of the vessel crystallization of the active hexol thiocyanate could be induced. This was recrystallized from the minimum volume of water containing a little ammonium thiocyanate, washed with ice-cold water, and dried in a vacuum. Generally, after two recrystallizations the isomer was obtained optically pure. The active form was less soluble in water than the racemic.

A 0·1% aqueous solution gave $[\alpha]_D$ +3·92°, $[\alpha]_{5461}$ +6·57°; whence $[\alpha]_D^{20°}$ +3920°, $[\alpha]_{5461}^{20°}$ +6570°, $[M]_D^{20°}$ +41,700°, $[M]_{5461}^{20°}$ +69,900 (Found: Co, 22·2; C, 20·6; H, 5·1; N, 23·9%. Calc. for $[Co_4(C_2N_2H_8)_6(OH)_6](CNS)_6.H_2O$: Co, 22·2; C, 20·3; H, 5·3; N, 23·7%).

(*e*) L$_{II}$-*Hexol* d-*Antimonyl Tartrate Nonahydrate*

To the solution left after precipitating D$_I$-hexol *d*-antimonyl tartrate a solution of potassium *d*-antimonyl tartrate (5 g) in hot water (25 ml) was carefully added in three equal portions so as to obtain three fractions. The conditions of precipitation were the same as those for D$_I$-hexol diastereoisomer. The rotation of the first fraction was *dextro* and third *laevo*, this being the L$_{II}$-hexol *d*-antimonyl tartrate. It was washed with water, ethanol, and ether and air-dried. A 0·1% aqueous solution gave $[\alpha]_D$ −2·50° (Found: C, 16·5; H, 3·5; N, 6·4%. Calc. for $[Co_4(C_2N_2H_8)_6(OH)_6](C_4H_4O_7Sb)_6.9H_2O$: C, 16·8; H, 3·7; N, 6·5%).

(*f*) L$_{II}$-*Hexol Thiocyanate Monohydrate*

L$_{II}$-Hexol *d*-antimonyl tartrate was converted to the active thiocyanate in the same manner as above. In this case, also, the active form was less soluble than the racemic. A 0·1% aqueous solution gave $[\alpha]_D$ −3·62°, $[\alpha]_{5461}$ −5·90°; whence $[\alpha]_D^{20°}$ −3620°, $[\alpha]_{5461}^{20°}$ −5900°; $[M]_D^{20°}$ −38,500°, $[M]_{5461}^{20°}$ −62,800° (Found: Co, 22·1; C, 20·7; H, 5·1; N, 23·9%. Calc. for $[Co_4(C_2N_2H_8)_6(OH)_6](CNS)_6.H_2O$: Co, 22·2; C, 20·3; H, 5·3; N, 23·7%).

* All rotations were measured in a 1 dm tube immediately after preparation.

(*g*) L_I-*Hexol* l-*Antimonyl Tartrate Octadecahydrate*

This was prepared in exactly the same way as D_I-hexol *d*-antimonyl tartrate, using potassium *l*-antimonyl tartrate. A 0·1% solution in water gave $[\alpha]_D$ −2·98° (Found: C, 15·7; H, 4·0; N, 6·0%. Calc. for $[Co_4(C_2N_2H_8)_6(OH)_6](C_4H_4O_7Sb)_6.18H_2O$: C, 15·8; H, 4·2; N, 6·1%).

(*h*) L_I-*Hexol Thiocyanate Monohydrate*

This was prepared from L_I-hexol *l*-antimonyl tartrate diastereoisomer in exactly the same manner as for the D_I-hexol. A 0·1% solution in water gave $[\alpha]_D$ −3·92°, $[\alpha]_{5461}$ −6·65°; whence $[\alpha]_D^{20°}$ −3920°, $[\alpha]_{5461}^{20°}$ −6650° (Found: Co, 22·0; C, 20·7; H, 5·2; N, 23·7%. Calc. for $[Co_4(C_2N_2H_8)_6(OH)_6](CNS)_6.H_2O$: Co, 22·2; C, 20·3; H, 5·3; N, 23·7%).

(*i*) D_{II}-*Hexol* l-*Antimonyl Tartrate Nonahydrate*

This was obtained from the solution left after precipitation of the L_I-diastereoisomer in exactly the same manner as in the isolation of the L_{II}-diastereoisomer using potassium *l*-antimonyl tartrate. A 0·1% solution in water gave $[\alpha]_D$ +1·80° (Found: C, 17·1; H, 3·6; N, 6·4%. Calc. for $[Co_4(C_2N_2H_8)_6(OH)_6](C_4H_4O_7Sb)_6.9H_2O$: C, 16·8; H, 3·7; N, 6·5%).

(*j*) D_{II}-*Hexol Thiocyanate Monohydrate*

This was prepared from D_{II}-hexol *l*-antimonyl tartrate diastereoisomer in the same manner as L_{II}-hexol thiocyanate. A 0·1% solution in water gave $[\alpha]_D$ +3·62°, $[\alpha]_{5461}$ +6·07°; whence $[\alpha]_D^{20°}$ +3620°, $[\alpha]_{5461}^{20°}$ +6070 (Found: Co, 22·1%. Calc. for $[Co_4(C_2N_2H_8)_6(OH)_6](CNS)_6.H_2O$: Co, 22·2%).

(*k*) *Rates of Racemization*

The rates of racemization were measured for the four forms isolated, at 40 °C. It was found that, neglecting the first few readings, the plot of $\log_{10}\alpha$ against time was a straight line for all four forms. Thus, the overall reaction followed first-order kinetics. The rotations observed for aqueous solutions of the four isomers at regular intervals are given in Tables 2 to 5.

TABLE 2

RACEMIZATION OF ISOMER D_I

Time (hr) ..	0	0·5	1·0	1·5	2·0	2·5	3·0	3·5
Rotation	2·74	2·35	2·01	1·64	1·40	1·15	0·89	0·73
$k_{40\,°C}$ *	$0·11\times10^{-3}$							

* The rate constant $k_{40\,°C}$ was determined (in sec^{-1}) from the plot of $\log_{10}\alpha$ against time.

TABLE 3

RACEMIZATION OF ISOMER L_I

Time (hr) ..	0	0·5	1·0	1·5	2·0	2·5	3·0	3·5
Rotation	2·30	2·00	1·74	1·47	1·11	0·87	0·71	0·65
$k_{40\,°C}$ *	$0·10\times10^{-3}$							

* See footnote to Table 2.

TABLE 4

RACEMIZATION OF ISOMER D_{II}

Time (hr) ..	0	0·5	1·0	1·5	2·0	2·5	3·0	3·5
Rotation	3·22	3·17	3·12	3·05	2·99	2·94	2·88	2·83
$k_{40\,°C}$ *	$0{\cdot}95\times10^{-5}$							

* See footnote to Table 2.

TABLE 5

RACEMIZATION OF ISOMER L_{II}

Time (hr) ..	0	0·5	1·0	1·5	2·0	2·5	3·0	3·5
Rotation	3·01	2·97	2·91	2·85	2·78	2·71	2·66	2·61
$k_{40\,°C}$ *	$0{\cdot}11\times10^{-4}$							

* See footnote to Table 2.

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PYROLYTIC CARBON FILMS FROM ETHYL CHLORIDE

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Summary

The formation of pyrolytic carbon films during the gas phase decomposition of ethyl chloride at 450 °C has been followed by measurement of the electrical conductance. On fresh glass surfaces there was observed an initial induction period of approximately 30 min after which the conductance rose steadily, the rate of change decreasing as ethylene accumulated in the system. The time of induction varied with surface treatment and has been attributed largely to the removal of some substance (e.g. water or oxygen) from the glass surface. Pressure measurements indicated no appreciable induction effect for the simultaneous decomposition of the ethyl chloride to ethylene and hydrogen chloride.

The films of carbonized material were semiconductive and their electrical resistance was estimated to be very much greater than that of graphite. (One film had an estimated specific resistance of 12 Ω cm at room temperature.) The electrical properties of the films were found to vary greatly with changes in the film thickness, the temperature, the applied voltage, and the pressure of the gases in contact with them. For these reasons the conductance measurements did not provide an accurate estimate of the amount of carbon deposited although they did provide information concerning the physical and chemical nature of the deposit. The behaviour of the films was consistent with the presence of a high concentration of " foreign " atoms, groups, and/or molecules at the intercrystal boundaries, as suggested by other workers.

The efficiency of these films in suppressing heterogeneous reactions is discussed in terms of the formation of a continuous non-polar coating on the surface of the glass.

I. INTRODUCTION

It is a matter of common observation that the gas phase pyrolysis of organic compounds is frequently accompanied by the deposition of a carbonized film on the walls of the containing vessel. Some substances such as allyl bromide (Maccoll 1955) and allyl chloride (Goodall and Howlett 1954) produce particularly heavy deposits. Brearley, Kistiakowsky, and Stauffer (1936) while investigating the kinetics of the decomposition of gaseous *tert.*-butyl and *tert.*-amyl chlorides noted that the heterogeneous reaction taking place on the walls could be suppressed by first allowing a fine coating of carbonized material to form on the glass surface. The " usefulness " of this deposit was found to be adversely affected by prolonged pumping under vacuum or by allowing oxygen to come into contact with the film, particularly at elevated temperatures.

The coating procedure has now become a standard technique in gas kinetics (Daniels and Veltmann 1939; Jones and Taylor 1940; Barton and Howlett

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1949*a*; Agius and Maccoll 1955). In a recent study by Swinbourne (1958) the carbonized deposit was formed by keeping the reaction vessel in contact with decomposing ethyl chloride at 450 °C for about 10 days, during which time 50–100 fresh additions of ethyl chloride were made. The purpose of the present investigation was to use electrical conductance measurements in order to gain information concerning the properties of the films so deposited. (For convenience, we shall refer to this type of film as " pyrolytic carbon ".)

Parallel to the layer planes, pure crystalline graphite at room temperatures has a specific resistance of about 4×10^{-5} Ω cm and shows a positive temperature coefficient (dR/RdT) of 0·009/°C. Perpendicular to the layer planes the specific resistance is of the order of 0·01 Ω cm* with a negative temperature coefficient of 0·04/°C (Washburn 1915; Pirani and Fehse 1923; Grisdale, Pfister, and van Roosbroeck 1951). X-Ray evidence suggests that within the crystallites of pyrolytic carbon, the atoms are arranged in layers in much the same way as they are in graphite, but that the layers are randomly stacked one upon the other instead of in a definite geometrical pattern as in graphite (Riley 1940; White and Germer 1941; see, however, Garten and Weiss 1957, p. 71). The electrical properties of pyrolytic carbons are greatly dependent upon their conditions of preparation. Those produced by the pyrolysis of organic substances below 600–700 °C are semiconductors with a specific resistance generally very much greater than 1×10^{-2} Ω cm. Mrozowski (1952*a*, 1952*b*) has attributed this semiconductivity to three main factors, namely, (i) " the scattering of electrons due to thermal lattice vibrations and to the boundaries of molecular planes ", (ii) " the presence of a finite energy gap between the filled and the conduction bands, the energy gap steadily decreasing with increase of molecular size ", and (iii) the removal, by heating, of " foreign " atoms (for example, hydrogen) or groups from the peripheries of the crystallites—such atoms or groups act as an " opaque barrier " to the passage of charges across the crystallite boundaries. The last factor must be of overwhelming importance in the case of " carbon " prepared at low temperatures (e.g. below 500 °C). At temperatures above 700–800 °C most of the foreign peripheral atoms or groups have been lost by the carbons, and Mrozowski then considers that the solids are " built of very small (20–30 Å dia.) turbostatic crystallites of graphite—packs of parallel graphite planes having no directional relationship to each other. Only at considerably higher temperatures, when the molecular planes reach a diameter of about 150 Å, a rotation starts to bring the planes into a regular directional arrangement and into a consecutive order corresponding to the large crystals of graphite."

II. Experimental

(*a*) *Reagent*

Ethyl chloride, B.P. anaesthetic grade (Woolwich-Elliott Chemical Co., Sydney) was used directly, without further purification. Before being admitted to the pyrolysis chamber, the reagent was thoroughly outgassed under vacuum.

* Krishnan and Ganguli (1939) have reported a value as high as 1 to 2 Ω cm.

(*b*) *Apparatus and Experimental Technique*

The pyrolyses were carried out in a Pyrex glass reactor *c.* 5 in. long by $1\frac{3}{4}$ in. diameter, housed in a high temperature thermostat constructed of brass and heated electrically (see Fig. 1). Within the region of the reactor the temperature was held constant to within ± 1 °C of the desired value by means of a modified form of the control system described by Thomas and Egloff (1941), a calibrated chromel-alumel thermocouple being used for temperature measure-

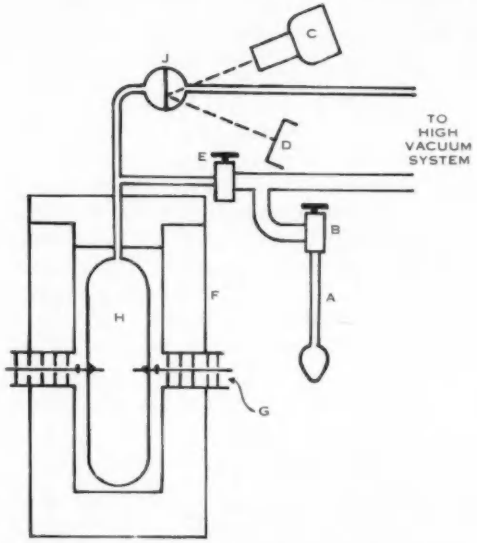


Fig. 1.—Pyrolysis chamber and auxiliary apparatus.
A, Ethyl chloride reservoir; *B*, *E*, high vacuum stopcocks; *C*, galvanometer lamp; *D*, ground screen; *F*, high temperature thermostat; *G*, mica disks; *H*, reaction vessel; *J*, glass membrane manometer.

ment. (Calibration was effected by checking against a rare-metal couple tested by the National Standards Laboratory, Sydney.) Capillary Pyrex leads connected the reaction vessel to an all-glass membrane manometer *J* (Swinbourne 1958) and via a stopcock *E* to a conventional high vacuum system.

The electrical resistance of the carbon films was measured between two tungsten wires sealed with C9 glass into opposite sides of the reactor. Leads from these wires were connected to the D.C. circuit shown in Figure 2. A series of mica disks (*G*, Fig. 1) fitted into holes through the furnace block served for electrical insulation of the leads and thermal insulation of the reactor. The circuit was designed as in Figure 2 to maintain at all times a fixed D.C. potential between the tungsten wires (see later explanation). Potential was applied by means of radio " B " batteries, the remainder of the circuit consisting of a double-

pole-double-throw switch S, two equivalent standard 2000 $\Omega \pm 0{\cdot}2$ per cent. resistances, R_2, R_4, and standard 10 $M\Omega \pm 0{\cdot}2$ per cent. resistance R_3. A Cambridge portable potentiometer modified for use with an external Cambridge spot galvanometer was used for measuring the potentials developed across R_2 and R_4. With the switch in position 1, and then in position 2, the voltage drops (E_2) across R_2 and (E_4) across R_4 respectively could be measured : the resistance R_1 between the tungsten electrodes was then given as $10E_4/E_2$ $M\Omega$ since R_2 and R_4 were small in comparison with R_1 and R_3.

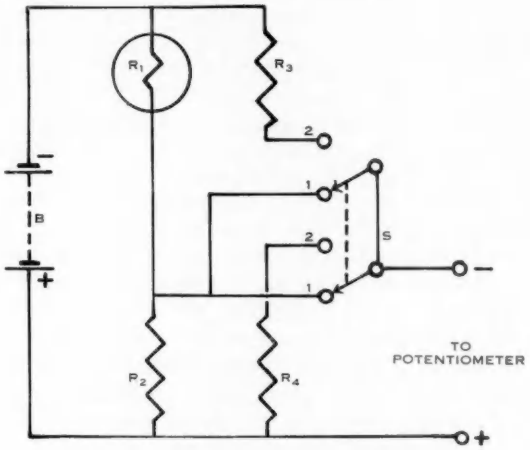


Fig. 2.—Electrical circuit for measurement of conductance. B, Radio battery (90, or 45, or 22½ V) ; S, double-pole-double-throw switch ; R_1, reaction vessel ; R_3, resistor, 10 $M\Omega \pm 0{\cdot}2$ per cent. ; R_2, R_4, resistors, 2000 $\Omega \pm 0{\cdot}2$ per cent.

Before a run, the reaction vessel was evacuated to a pressure of the order of 10^{-3} to 10^{-4} mm with a two-stage rotary oil pump, and D.C. potential from the bridge was then applied to the tungsten electrodes. At 450 °C the resistance of the glass between the electrodes was about 2 MΩ at the instant of application of the voltage, but increased to a value in excess of 200 MΩ in about 2 hr. This effect has been described by Stanworth (1950, pp. 124–33) as being due to polarization-migration of sodium ions to the cathode with a consequent build-up of a silica-rich zone around the anode.* When the resistance of the glass had built up to a high value (generally above 200 MΩ), ethyl chloride was quickly admitted to the reaction chamber through tap E (as shown in Fig. 1) to give a

* Because of these local changes in composition there was a tendency for breakdown of the glass-to-metal seals (generally at the cathode) when the potential was applied over prolonged periods (e.g. over 12 hr). This presented a time limit to the observation of changes in conductance of the films. In order to extend the life of a flask, it was found necessary to short-circuit the electrodes at the end of a run and before cooling.

total pressure of 250 mm, and a stopwatch was started. At frequent intervals, the resistance between the tungsten electrodes was measured and, by noting the pressure required to balance the glass membrane manometer, the extent of the decomposition of the ethyl chloride to ethylene and hydrogen chloride was determined. The films were observed to have a highly negative temperature coefficient of resistance and for this reason it was found necessary to take readings always at the same point of the thermal cycle of the thermostat.

The removal of the film was achieved by first evacuating the reactor and then allowing it to come into contact with air at 450 °C until the resistance was constant at a high value, at which stage it was assumed that all carbonaceous material had been removed.

III. Results

Except in a few instances, all runs were carried out at 449 °C with 250 mm initial pressure of ethyl chloride. The values recorded represent the conductance $(M\Omega)^{-1}$ as measured between the electrodes, suitable correction having been made for the conductance of the glass (except in the early stages of a run, this correction was of negligible magnitude). However, tests on a suitably shaped Bakelite strip coated with a conducting varnish indicated that these values were almost identical* with the conductivity in $(M\Omega)^{-1}/cm^2$.

Figure 3 shows the results of three typical runs on fresh glass surfaces at 449 °C with different voltages applied across the electrodes. In all cases there was a marked induction period after which the conductance increased rather rapidly for about 60 min. At this stage, when about 70 per cent. of the ethyl chloride had decomposed, the conductance changed less rapidly with time. With fresh glass surfaces the period of induction, although rather irreproducible, was approximately 30 min, but could be almost entirely eliminated by admitting 30 mm of ethyl chloride, and immediately pumping out once more, before starting a run. New reactors washed with distilled water† tended to show very lengthy induction periods, and it seems likely, therefore, that this phenomenon may be associated with the removal of some substance (e.g. water or oxygen) from the walls of the reactor.

When the reactor was evacuated at the conclusion of a run, it was noticed that the conductance of the film increased greatly as the pressure was reduced, (see Fig. 4), the effect being *relatively* greater for films of low conductance (i.e. presumably thin films). The values shown in Figure 4 were obtained by holding each pressure constant for 5 min before the corresponding electrical measurement was made; the curves must be considered as approximate only as the resistance still continued to change slowly after the system had been pumped out to a low pressure. When fresh ethyl chloride was admitted to a reactor already coated with a carbonaceous film there was an immediate drop followed by a rapid increase in conductance, as shown in Figure 5. In all cases, the accumulation of large amounts of ethylene in the system was accompanied by a decrease

* The estimated conversion was: conductivity $(M\Omega)^{-1}/cm^2$ = measured conductance/1·14.

† The reactor surface received no special chemical treatment prior to use.

in the rate of change of conductance. It therefore seems likely (but by no means definite) that pyrolytic carbon was deposited more slowly from ethylene than from ethyl chloride.

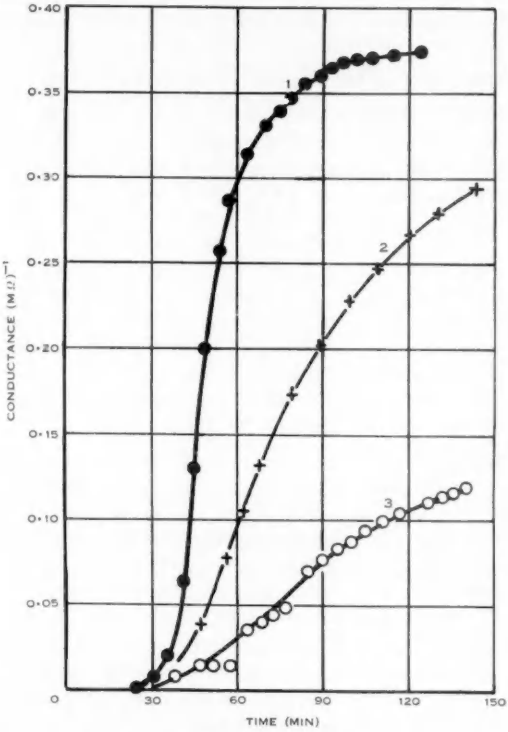


Fig. 3.—Changes in film conductance during formation from ethyl chloride at 449 °C.

Three typical pyrolyses on fresh glass surfaces:

● 90 V applied between electrodes;
\+ 45 V applied;
○ 22½ V applied.

(250 mm initial pressure of ethyl chloride in each case.)

It is interesting to note (see Fig. 3) that the application of a high potential between the electrodes during pyrolysis increased the *measured* conductance of the film formed.* This could largely be explained in terms of the films

* There was some evidence that the "true" conductance of a film may have been affected by the application of a D.C. potential during its formation. For example, a film formed by pyrolysis, without the application of a potential for the first 12 hr, gave a conductance measurement of only 0·05 $(M\Omega)^{-1}$ after 22½ V had been applied for ½ hr.

behaving as non-linear resistors (i.e. not obeying Ohm's law, for example, the measured conductance of a film *under vacuum* at 449 °C was $0{\cdot}444\ (M\Omega)^{-1}$ with $22\frac{1}{2}$ V applied, $0{\cdot}486\ (M\Omega)^{-1}$ with 45 V, and $0{\cdot}521\ (M\Omega)^{-1}$ with 90 V).

The effect of temperature upon the conductance curves was briefly examined. Figure 6 shows the change in conductance with time for typical pyrolyses on

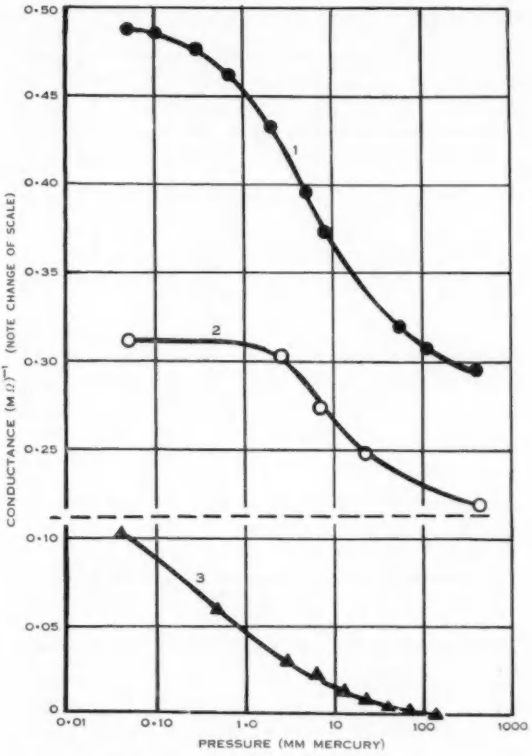


Fig. 4.—Effect of gas pressure on conductance of pyrolytic carbon films.

Films formed and measured at 449 °C:

- ● No. 1, 45 V applied between electrodes;
- ○ No. 2, $22\frac{1}{2}$ V applied between electrodes;
- ▲ No. 3, $22\frac{1}{2}$ V applied between electrodes.

fresh glass surfaces previously flushed with ethyl chloride (to shorten induction periods) at 410, 429, and 449 °C (90 V applied voltage). The curves are all of the same general shape, and, as expected, the conductance increased more rapidly at higher temperatures. The temperature *coefficient* of resistance was also checked for three films of varying thicknesses (see Table 1). Indications

were that the temperature *coefficient* of resistance : (i) increased with a decrease in the film thickness, and (ii) increased with a decrease in temperature. The effect of environment upon the coefficient of resistance of a common film was not closely examined.

In contrast to the film conductance readings shown in Figure 3, the manometer readings indicated no significant periods of induction in the overall decomposition of the ethyl chloride to ethylene and hydrogen chloride. Pressure

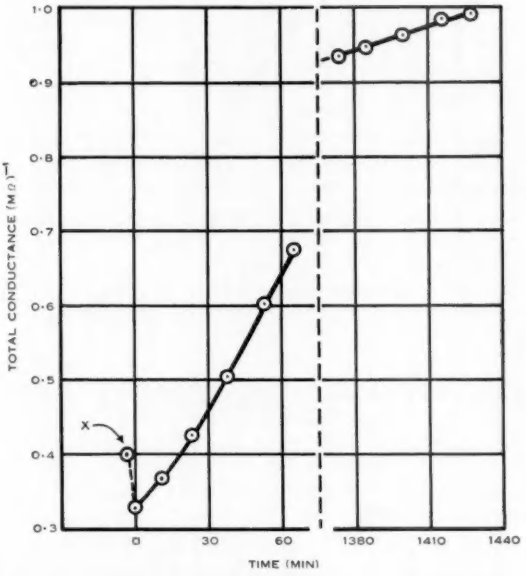


Fig. 5.—Deposition of pyrolytic carbon on a previously formed film.
Temperature 449 °C, 22½ V applied, except between 70 and 1300 min, when no voltage was applied between the electrodes.
×, Conductance of evacuated film immediately prior to admission of ethyl chloride.

readings for runs at 449 °C are shown in Figure 7. From these curves it may be observed that the velocity decreased as the film increased in thickness. The dotted line represents the rate of pyrolysis at 449 °C in well-coated reactors, as estimated from the studies of Barton and Howlett (1949*b*).

Examination of the carbonized films showed them to be apparently uniformly distributed over the glass surface in the reaction zone. One film deposited at 449 °C with a measured resistance of 3·16 MΩ (90 V, D.C.) in air at room temperature was found to have an optical density of approximately 0·39 (tungsten source). Agar (1957) has demonstrated that a nearly linear relationship exists between the optical density and the thickness of evaporated carbon

films : an optical density of 0·39 would correspond to a film thickness of 330 Å. Assuming the optical properties of the films formed in the present study do not differ too greatly from those studied by Agar, this thickness would yield a specific resistance of 12 Ω cm for the above film at room temperature. (Goldberg

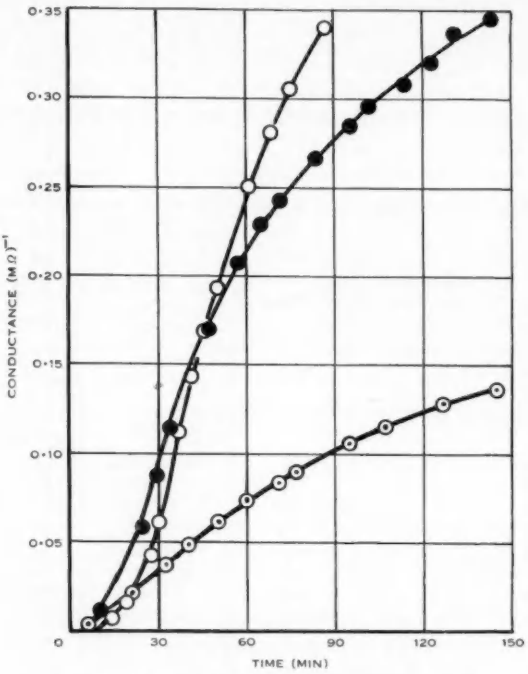


Fig. 6.—Film formation at various temperatures.
Induction period shortened by preliminary flushing with ethyl chloride.

○ 449 °C, 90 V applied, 250 mm initial pressure.
● 429 °C, 90 V applied, 250 mm initial pressure.
⊙ 410 °C, 90 V applied, 250 mm initial pressure.

and Daniels 1957 examined the film deposited after 5 months of experimenting with decomposing ethyl bromide at about 400 °C. It was found to have a resistance of 15,000 Ω/cm² and to be " less than 2 μ thick ". A thickness of 2 μ would yield a specific resistance of 3 Ω cm.)

IV. Discussion

From these preliminary studies it is quite evident that electrical conductance measurements do not, in themselves, provide an accurate estimate of the *amount* of carbon deposited. The electrical properties of the films depend too largely upon the film thickness, the temperature, the applied voltage, and the pressure

of the gases in contact with the films. However, when used in conjunction with other measurements (e.g. optical density) the conductance may furnish interesting information concerning the *structure* or changes in the physical and chemical nature of the carbonized deposit associated with differing conditions of deposition.

The high specific resistance of the deposits as compared with graphite, the marked decrease in this resistance as the gas pressure is reduced, and the semiconductivity are all properties consistent with the presence of a high concentration of "foreign" atoms, groups, and/or molecules. The sudden increase in resistance as gas is readmitted suggests that these substances are

TABLE 1

TEMPERATURE COEFFICIENT OF RESISTANCE OF PYROLYTIC CARBON FILMS

Resistance of Film in Reaction Products at 449 °C (MΩ)	Temperature Range over Which Change in Resistance was Tested (°C)	Film Environment When Tested	Temperature Coefficient of Resistance (°K)$^{-1}$
Applied potential 22½ V, D.C.			
0·186	37–97	In reaction products	—0·0080
0·186	370–410	In reaction products	—0·0050
0·186	410–450	In reaction products	—0·0033
0·485	370–410	Evacuated	—0·0049
0·485	410–450	Evacuated	—0·0035
Applied potential 90 V, D.C.			
2·93	410–450	Evacuated	—0·019

mainly present at the intercrystal boundaries, as suggested by Mrozowski (1952*a*, 1952*b*) and Grisdale, Pfister, and van Roosbroeck (1951). Complete absence of oxygen rules out the possibility, in this case, of the semiconductivity being due to the presence of "chromene" groups (see Garten and Weiss 1957, p. 108; Garten, Weiss, and Willis 1957, p. 304).

Such films, therefore, effectively cover the walls of the vessel with an essentially non-polar "skin", thereby suppressing heterogeneous reactions which might otherwise occur on the highly polar glass surface. The continuous nature of the coating is probably destroyed by prolonged pumping under vacuum due to the exhaustive removal of the foreign substances concentrated at the intercrystal boundaries, with consequent shrinkage of the film and the formation of microcracks etc. It seems likely that the proportion of foreign substances

would be larger in the case of very thin films as these were observed to have the greater variation of electrical resistance with changes in temperature or pressure.

The usefulness of the films in suppressing heterogeneous reactions is detrimentally affected by allowing them to come into contact with oxygen gas. It is sometimes difficult to return them to a " useful " condition by the further deposition of carbonized material (Brearley, Kistiakowsky, and Stauffer 1936 ;

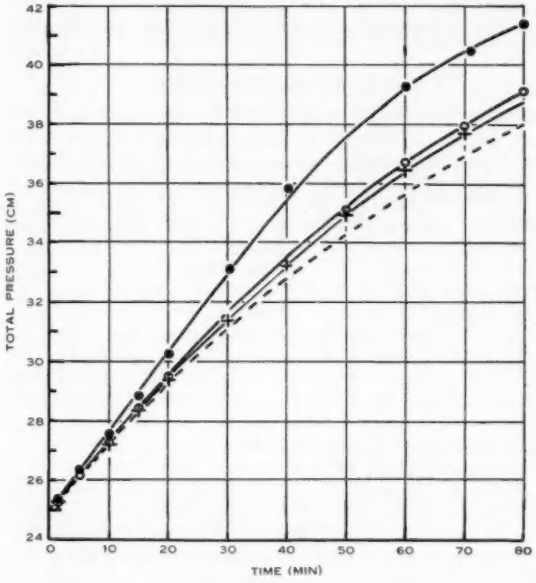
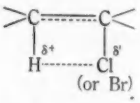


Fig. 7.—Rate of decomposition of ethyl chloride to ethylene and hydrogen chloride at 449 °C.

● In an untreated reactor (fresh glass) ; ○ in a reactor kept in contact with ethyl chloride and decomposition products at 449 °C for 24 hr ; + in a reactor kept in contact with ethyl chloride and decomposition products at 449 °C for 44 hr ; - - estimated rate in a well-coated reactor at 449 °C (from the studies of Barton and Howlett 1949*b*). (250 mm initial pressure in each case.)

Barton and Howlett 1949*a*, p. 157 ; Barton and Onyon 1949, p. 726 ; Swinbourne 1958, p. 318). Incorporation of oxygen into the structure of pyrolytic carbon results in the formation of polar groups of various types as extensively discussed by Garten and Weiss (1957). Maccoll and Thomas (1955) and Ingold (1957) have suggested that in gas-phase pyrolyses resulting in the unimolecular elimination of hydrogen chloride, or hydrogen bromide, the transition state is one

involving extensive polarization of the carbon-halogen bond as in the S_N1 mechanism in solution:



By an extension of this argument the catalytic activity of substances such as glass and oxygenated pyrolytic carbon may be largely accounted for by the polar groups on the surface assisting the separation of charges within the reacting molecules.

V. Acknowledgments

The authors acknowledge with thanks advice on the measurement of resistance given by Mr. P. Russell of International Resistance Co. (Australasia) Ltd. One of us (C.C.K.) wishes to express his gratitude to the Directors of International Resistance Co. and to Professor R. C. L. Bosworth for the opportunity to undertake this research at the University of New South Wales.

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THE SULPHIDES, SELENIDES, AND TELLURIDES OF TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM

I. PREPARATION AND CHARACTERIZATION

By F. K. McTaggart* and A. D. Wadsley*

[*Manuscript received May* 15, 1958]

Summary

The nine systems Ti-S, Ti-Se, Ti-Te, Zr-S, Zr-Se, Zr-Te, Hf-S, Hf-Se, and Hf-Te have been investigated by X-ray techniques for the occurrence of phases between the compositions $AX_{max.}$ and AX. Compounds were prepared from materials of high purity by direct synthesis from the elements, or by degradation of a higher to a lower phase. All manipulation was done in dry argon. Several new compounds are reported, some major differences in the type of phase formed by zirconium and hafnium are noted, and a different interpretation of the X-ray data for the AX_2 compounds is discussed.

I. Introduction

We have for some time been interested in the chemistry, structure, properties, and stoicheiometry of the sulphides, selenides, and tellurides (that is, the chalcogenides) of the Group IV metals Ti, Zr, Hf, and Th. Whilst a number of combinations of these metals with the chalcogens were synthesized by early workers, it was not until the use of vapour pressure isotherms and X-ray diffraction analysis that such systems could be properly defined. However, an examination of the recent literature has disclosed many inconsistencies. There are gaps in the knowledge of the phases present in some systems and where data exist there are often considerable differences of opinion. As recently as September 1957, during the writing of this paper, Hahn and Ness (1957*a*) in reporting the Zr-Se and Zr-Te systems, apparently overlooked the fact, as others have done, that the crystals of the AX_2 compounds usually exist in the twinned form. A study of the modes of preparation of, materials used in, and chemical analyses of the compounds which have been described also led us to believe that as a preliminary to more particular studies, a general reappraisal of the systems was desirable.

The present paper discusses the preparation, analysis, and description of phases at certain fixed points in what now appear to be systems containing several non-stoicheiometric phase regions, but no attempt has been made accurately to define composition limits. Additional papers will appear in which chemical and physical properties will be described in more detail.

Data for the thorium chalcogenides will be the subject of a separate paper.

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II. Experimental

(*a*) *Materials*

The sulphur, selenium, and tellurium which were B.D.H. laboratory grade were purified by distillation, the last two under vacuum, and the first and last fractions were discarded. Titanium and zirconium metals of 99·6 and 99·8 per cent. purity, kindly made available to us by the U.S. Bureau of Mines, were reduced to filings of −150 mesh, carefully freed from iron, degreased in light petroleum, and washed with dilute acid. Hafnium metal in powder form was the best commercial grade available and contained not less than 99·5 per cent. hafnium together with approximately 0·5 per cent. zirconium.

(*b*) *Methods of Preparation*

(i) To prepare the higher chalcogenides provision was made for separately heating the reactants by suitable design of the vessel. For quantities up to 100 g the metal was evenly spread out in shallow silica boats placed in clear silica tubes to which an additional limb containing an excess of the non-metal was sealed at an angle of about 20°. For smaller quantities a different type of reaction tube, illustrated by Figure 1, was used. In both cases the tubes were sealed after outgassing to 0·0002 mm or better, the metal was thoroughly heated and the non-metal fused. The portion of the tube containing the metal was then heated to the desired temperature fairly rapidly, but the temperature of the non-metal was raised slowly until reaction was initiated and the rate of reaction was controlled by adjusting this temperature. Finally, the temperature of the chalcogen was brought to a value such that the pressure inside was approximately atmospheric and the tubes were then left for several weeks. Excess chalcogen was then sublimed away from the reaction products by heating to 350°C for sulphides, 450°C for selenides, and 550°C for tellurides with the other end of the tube at room temperature.

(ii) Direct reaction between accurately weighed quantities of both elements in synthesis tubes of the second type was the preferred method for synthesis of compounds containing less than the maximum non-metal–metal ratio. After degassing, the sealed evacuated tubes were heated slowly (6 hr to 2 days) and homogeneously to the desired temperature and then held for 5 to 7 days. The contents were then ground and reheated for a similar period. Additional grinding and heating cycles were made, if necessary, until equilibrium was reached. We preferred heating for long periods at a relatively low temperature in order to prevent diffusion of oxygen through the silica, which at high temperatures can result in oxidation of the chalcogenide.

(iii) Degradation, the decomposition of a higher chalcogenide to a lower one, was carried out in long clear silica tubes evacuated and sealed after careful outgassing. The end containing the charge was slowly raised to temperature whilst the other was held at room temperature. The decomposition was complete when no further sublimation occurred and this could be checked by pulling the tube an inch or so further out of the furnace and inspecting after a

suitable interval for newly formed sublimate. If the composition of the original charge was known, the weights of sublimate and residual chalcogenide gave an accurate indication of the composition of the latter, and no further chemical analysis was considered necessary.

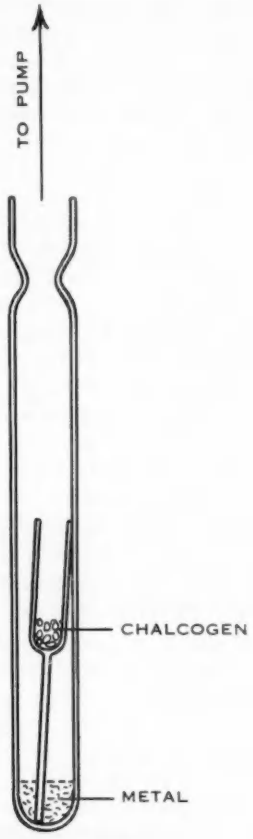

Fig. 1.—Reaction tube.

(*c*) *Storage and Handling*

Most of the compounds undergo oxidation to a greater or lesser extent in air. The AX compounds are usually the most reactive, TiTe for example, being pyrophoric. Of the AX_2 phases ZrS_2 can absorb up to 0·5 per cent. by weight of oxygen, and even the trichalcogenides AX_3 undergo some change on long exposure. All preparations were therefore manipulated and stored in an atmosphere of dry argon.

(*d*) *Methods of Chemical Analysis*

(i) *Sulphur, Selenium, and Tellurium.*—Sulphur analyses were done for us by Dr. W. Zimmermann* using the potassium fusion method developed by him (Zimmermann 1943, 1946, 1950, 1952) as a microanalytical method for materials of a widely differing nature. In contrast to many older techniques the extraction of sulphur is complete. The method is readily applicable to selenides and tellurides also.

These latter compounds may however be analysed for selenium and tellurium in the following manner: The compound is oxidized to SeO_2 or TeO_2 together with the metal oxide, at an elevated temperature. SeO_2 sublimes above about 320°C and can be collected and weighed directly providing precautions are observed to prevent the access of moisture. TeO_2 which does not sublime readily even at much higher temperatures is reduced by hydrogen at 700°C to elemental tellurium which then sublimes and may be weighed directly. In this case several oxidation-reduction cycles may be necessary to free completely the metal oxide of its tellurium content. The oxidations in all cases are carried out in oxygen.

These two simple gravimetric procedures yielded results comparable in accuracy to the microanalytical method and were frequently used when the total analysis of a chalcogenide other than a sulphide was desired.

(ii) *Metals.*—For selenides and tellurides the metal content was usually estimated by weighing the oxide which was left after selenium or tellurium had been removed by volatilization in the above gravimetric procedure. The oxides were heated to 1000°C until constant weight was achieved. The metal content of all sulphides was determined by standard wet-way analytical methods.

In spite of the fact that these methods of analysis have been found most reliable, we do not claim an accuracy greater than $\pm 0{\cdot}1$ per cent. for any component, and atomic ratios (i.e. n in AX_n) are therefore not quoted to closer than $\pm 0{\cdot}05$.

(*e*) *Density*

Densities were determined by means of a pyknometer. The quantity of chalcogenide used was of the order of 0·5 g and this was pumped to approximately 0·1 mm pressure before being covered by toluene.

(*f*) *X-Ray Diffraction Examination*

All preparations were first examined by powder diffraction methods using a camera 14·4 cm in diameter, the film in the asymmetric position, and CuK_α radiation. The specimens were sealed into thin-walled Lindmann glass capillaries to prevent any possible oxidation during exposure. Where the diffraction patterns could be unambiguously indexed, the unit cell dimensions were determined by the extrapolation procedure of Taylor and Floyd (1950).

The symmetry and the approximate unit cell dimensions of those trichalcogenides which formed suitable crystals were found by Weissenberg and

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precession photography with Cu and Mo radiation respectively. More accurate dimensions were then determined from films exposed in a Guinier-type focusing camera.

III. Results and Discussion

(*a*) *The Trichalcogenides* AX_3

Table 1 summarizes the properties of the phases of formula AX_3 which were obtained.

Titanium forms a trisulphide below 560°C and a temperature of 480–500°C was normally used during preparation. When the metal is held at a temperature higher than 560°C, TiS_2 is formed. However in both cases filamentary ribbonlike crystals of the trisulphide, up to 1½ cm long, 0·5 mm wide, and 0·01 mm thick will form by sublimation in a region of the synthesis tube where the temperature is about 460°C. Biltz, Ehrlich, and Meisel (1937) first reported the TiS_3 phase. Our sublimed crystals (Plate 1) are apparently similar to those recently described by Hahn and Harder (1956). Despite a wide range of experimental conditions, no $TiSe_3$ or $TiTe_3$ could be prepared.

Zirconium readily formed all three trichalcogenides as crystals large enough for manipulation. The trisulphide formed at 600°C and when the temperature was raised to 700°C a crystalline sublimate slowly appeared on the cooler parts of the tube. These were much smaller than the TiS_3 crystals and resembled those reported by Strotzer, Biltz, and Meisel (1940). Hägg and Schönberg (1954) who were unable to prepare either TiS_3 or ZrS_3 appear to have used too high a temperature, but Hahn *et al.* (1957) confirmed this phase.

$ZrSe_3$ and $ZrTe_3$ were formed by heating the synthesis tubes homogeneously at 600°C. Unlike $ZrSe_3$, $ZrTe_3$ sublimed readily at 800°C. Hahn and Ness (1957*a*) recently reported these two phases.

HfS_3 formed as a fine powder when the metal was held at 570–600°C and the sulphur at 420–440°C. By increasing the temperature of the chalcogenide to 800°C and heating for several months, a small quantity of crystals sublimed. $HfSe_3$ was prepared only as a finely divided powder by heating the entire tube at 600°C. No $HfTe_3$ could be made.

The crystallographic data are given in Table 1. All the trichalcogenides are isomorphous with monoclinic symmetry, and where single crystal data could be obtained it was clear that the crystals of each compound were twinned on the (001) face. Since the only systematic absences were for $(0k0)$ with $k \neq 2n$ the space group was limited to $P2_1$ or $P2_1/m$. Hahn and Harder (1956) also gave this space group for TiS_3 and Hahn and Ness (1957*a*) showed the isomorphous relationships so far as the zirconium trichalcogenides were concerned. These authors gave $(00l)$ with $l \neq 2n$ as absent spectra which, however, are not required by this space group. They also gave *c*-axis dimensions which were twice our values, and evidently overlooked the possibility of twinning in their X-ray studies. The single crystal films of our AX_3 compounds invariably showed two sets of data arising from crystals of more or less unequal size twinned on the (001) face. The only other compound which bears any resemblance to these is

TABLE 1

CHEMICAL AND CRYSTALLOGRAPHIC DATA FOR THE TRICHALCOGENIDES AX_3

Compound	Composition					Appearance	Density ($g\ cm^{-3}$)		Crystal System	Unit Cell Dimensions (Å)				Space Group
	Theoretical		Observed				Obs.	Calc.		a	b	c		
	%A	%X	%A	%X	n									
TiS_3	32·24	66·76	33·5	66·3	2·95	Bluish black filamentous ribbons	3·22	3·25	Monoclinic	5·01	3·40	8·80	98·4°	$P2_1$ or $P2_1/m$
ZrS_3	48·66	51·34	49·1	50·7	2·95	Dark orange needles	3·78	3·82	,,	5·04	3·60	8·95	98·5°	,,
$ZrSe_3$	27·80	72·20	27·3	72·8	3·05	Purplish black ribbons	5·70	5·72	,,	5·42	3·74	9·45	98·2°	,,
$ZrTe_3$	19·24	80·76	19·6	79·3	2·90	Lustrous black needles	6·80	6·82	,,	5·89	3·93	10·10	98·4°	,,
HfS_3	64·99	35·01	65·5	35·0	3·00	Bright light orange powder	*	5·70	,,	5·08	3·68	8·96	98·4°	,,
$HfSe_3$	42·99	57·01	43·1	55·5	2·90	Purplish black powder	*	7·30	,,	5·48	3·72	9·47	98·3°	,,

* Insufficient material for accurate density measurements.

uranium triselenide described by Khodad and Flahaut (1957). A literature search failed to classify this group with any AX_3 compound for which the structure is known, and the atomic arrangement of $ZrTe_3$, at present in progress, will be reported in due course.

(*b*) *The Dichalcogenides* AX_2

Table 2 summarizes the methods of formation of the dichalcogenides together with chemical analyses and crystallographic constants. Each compound crystallizes in the hexagonal system, and whilst no structure factors have been calculated all obviously have the cadmium iodide structure (Strukturbericht classification *C6*). The new compounds recorded in Table 2 are HfS_2 and $HfSe_2$. The unit cell dimensions of the remainder are in good agreement with those given by previous workers.

A feature of the preparation of $TiTe_2$ was the readiness with which sublimation took place if the temperature of the metal end of the synthesis tube was allowed to rise above about 650°C. After a few days at 750°C the entire contents of a boat would sublime away.

$HfTe_2$ could not be prepared. Mixtures of the elements in the atomic ratio 1:2 after prolonged heating gave diffraction patterns of the *B8* type with additional tellurium lines. The removal of excess non-metal gave the upper composition limit of about $HfTe_{1\cdot6}$; this is reported in the next group.

Discrepancies between the observed and calculated densities led Ehrlich (1949) to suppose that whilst $TiSe_2$ and $TiTe_2$ were ostensibly stoicheiometric, the lattices in fact had equal numbers of vacancies of both elements and therefore still gave a formula AX_2. Our data do not support this view. On the other hand a formula $Zr_{1\cdot12}Te_{1\cdot90}$, which requires an excess of metal and a deficit of tellurium, leads to better agreement between densities for the substance $ZrTe_{1\cdot7}$, which resulted from the degradation of $ZrTe_3$ at 900°C. Possibly, therefore, at the stoicheiometric limit AX_2, the lattices of the *C6* type are quite regular, and for the intermediate compositions which can extend to $AX_{1\cdot7}$ or lower, additional metal ions, absent non-metal ions or both, may be found. We believe that the type of defect which is responsible is governed by the conditions of formation and that an extended thermal investigation, beyond our present interests, must eventually be made.

(*c*) *The Sesquichalcogenides*

All compounds in this group were prepared by direct interaction of the elements at 800°C, and the only ones hitherto unreported are the hafnium compounds.

The close similarities of structure found for both the AX_3 and the AX_2 groups are not found in the sesquichalcogenides (Table 3). Ti_2Se_3, Ti_2Te_3, Zr_2Te_3, Hf_2S_3, and Hf_2Te_3 all have hexagonal symmetry and are intermediate in structure between the *C6* and *B8* types. A model in which additional metal atoms randomly occupy the octahedral positions existing between adjacent non-metal sheets of the *C6* structure has been proposed for many of the sesquichalcogenide systems (Téngner 1938). These "phases" may then be

TABLE 2

CHEMICAL AND CRYSTALLOGRAPHIC DATA FOR THE DICHALCOGENIDES AX_2

Compound	Method of Preparation	Composition					Appearance	Density ($g\ cm^{-3}$)		Symmetry	Unit Cell Dimensions (Å)	
		Theoretical		Observed								
		%A	%X	%A	%X	n		Obs.	Calc.		a	c
TiS_2	Degradation of TiS_3 at 600 °C	42·75	57·25	43·4	56·5	1·95	Dark bronze	3·24	3·28	Hexagonal	3·39	5·70
$TiSe_2$	Interaction of elements 550–580 °C	23·27	76·73	23·3	76·5	2·00	Purplish brown crystals	5·26	5·26	,,	3·535	6·004
$TiTe_2$	Interaction of elements 580–620 °C	15·80	84·20	15·9	84·0	2·00	Black hexagonal plates	6·28	6·34	,,	3·76	6·48
ZrS_2	Degradation of ZrS_3 at 900 °C	58·72	41·28	58·8	40·9	2·00	Violet-brown	3·79	3·82	,,	3·662	5·813
$ZrSe_2$	Degradation of $ZrSe_3$ at 900 °C	36·61	63·34	36·9	63·0	1·95	Dark purplish brown	5·48	5·48	,,	3·770	6·137
$ZrTe_2$	Degradation of $ZrTe_3$ at 900 °C	26·33	73·67	29·4	70·5	1·70	Purplish brown	6·38	6·36†	,,	3·952	6·660
HfS_2	Degradation of HfS_3 at 900 °C	73·58	26·42	73·5	26·2	2·00	Light purplish brown	*	6·03	,,	3·635	5·837
$HfSe_2$	Degradation of $HfSe_3$ at 900 °C	53·07	46·93	54·0	44·2	1·85	Very dark brown	*	7·46‡	,,	3·748	6·159

* Insufficient material available for accurate density determinations.

† Calculated for the formula $Zr_{1\cdot12}Te_{1\cdot90}$ (see text).

‡ Calculated for $HfSe_2$ in view of analytical uncertainty.

TABLE 3

CHEMICAL AND CRYSTALLOGRAPHIC DATA FOR THE "SESQUICHALCOGENIDES" A_2X_3

Compound	Appearance	Density ($g\ cm^{-3}$)		Unit Cell Formula	Symmetry	Unit Cell Dimensions (Å)		Space Group	Structure Type
		Obs.	Calc.			*a*	*c*		
Ti_2S_3	Black	3·64	3·71	$Ti_{2\cdot67}S_4$	Hexagonal	3·43	11·42	$P6_3mc$	New
Ti_2Se_3	Black	5·29	5·48	$Ti_{1\cdot33}Se_2$	,,	3·595	5·994	—	*C6–B8*
Ti_2Te_3	Black	6·30	6·40	$Ti_{1\cdot33}Te_2$	,,	3·878	6·350	—	*C6–B8*
Zr_2S_3	Black	4·29	4·29	$Zr_{20}S_{30}$	Cubic	10·253		$P4_132$ or $P4_332$	Defective NaCl
Zr_2Se_3	Black	—	6·11	Zr_4Se_6	Hexagonal	3·757	18·63	—	New
Zr_2Te_3	Black	6·40	6·40†	$Zr_{1\cdot26}Te_{1\cdot90}$	,,	3·982	6·700	—	*C6–B8*
Hf_2S_3	Light yellow-brown	*	7·50	$Hf_{1\cdot33}S_2$	,,	3·635	5·839	—	*C6–B8*
Hf_2Se_3	Black	*	Complex diffraction pattern could not be indexed						
Hf_2Te_3	Black	*	9·14	$Hf_{1\cdot33}Te_2$	Hexagonal	3·947	6·635	—	*C6–B8*

* Insufficient material for accurate density determinations.

† Based on the assumption of a defective anion lattice.

TABLE 4

CHEMICAL AND CRYSTALLOGRAPHIC DATA FOR THE MONOCHALCOGENIDES AX

Compound	Appearance	Density ($g\ cm^{-3}$)		Unit Cell Dimensions (Å)		Symmetry	Remarks
		Obs.	Calc.				
TiS	Dark grey powder	4·2	4·46	$a=3·41$	$c=26·41$	Hexagonal	In agreement with Hahn and Harder (1956)
				$a=9·021$	$\alpha=21°\ 48'$	Rhombohedral	
TiSe	Black powder	5·7	6·34	$a=7·15$	$c=12·00$	Hexagonal	Dimensions from Hahn and Ness (1957*b*)
TiTe	„ „	6·4	7·14	$a=7·72$	$c=12·65$	Hexagonal	Dimensions from Hahn and Ness (1957*b*); pyrophoric
ZrS	„ „	4·6	4·56†	$a=10·25$		Cubic	
ZrSe	Dark brown powder	5·9					Absorbs oxygen rapidly. Present data gave a mixture of $Zr+ZrSe_2$
ZrTe	Black powder	6·6	6·48	$a=3·95$	$c=6·64$	Hexagonal	In agreement with Hahn and Ness (1957*a*); pyrophoric
HfS	„ „	*					
HfSe	„ „	*					Takes up oxygen rapidly
HfTe	„ „	*					

* Insufficient material for density determinations.

† Based upon a unit cell $Zr_{24}S_{21}$.

TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM CHALCOGENIDES. I

Sublimed crystals of TiS_3 (×2).

regarded as unique compositions in non-stoicheiometric compounds of wide composition limits. The values calculated for the densities in Table 3 are based upon the unit cell formulae given there. Whilst there is some measure of disagreement, it should be emphasized that several phases oxidize readily, and although considerable care was exercised with the density measurements it is probable that the values quoted are somewhat low. Zr_2Te_3 again occupies an anomalous position and it would seem that this alone of the hexagonal phases can with some certainty be said to agree with Ehrlich's hypothesis of a defective anionic lattice.

Ti_2S_3 has a diffraction pattern containing many more lines than that of TiS_2, requiring a doubled *c*-axis. The structure, which is now known (Hahn and Harder 1956; Wadsley 1957), persists over the composition range Ti_3S_4–$Ti_{2.7}S_4$.

Zr_2S_3 gave data in good agreement with that of Strotzer, Biltz, and Meisel (1940). The pattern indexes as a primitive cubic unit cell of side 10·25 Å, all reflections save three derived from a face centred cubic lattice. The only systematic absences are for *h*00 etc. with $h \neq 4n$ giving $P4_132$ or $P4_332$ as possible space groups. The pattern, with minor variations of line intensity, persists over the range from Zr_5S_8 to Zr_9S_8. This substantially confirms the recent work of Hahn *et al.* (1957) who proposed a structure for Zr_2S_3 based upon that of NaCl with vacancies in the sulphur lattice randomly distributed over the entire structures and vacancies in the metal sites confined to one particular sixteenfold set. Our diffraction data are, however, of lower symmetry than theirs suggesting that further ordering processes occur. These differences possibly reflect the thermal history of the specimens.

The diffraction pattern of Zr_2Se_3 contained several lines of strong intensity in addition to those common to $ZrSe_2$, and could be assigned indices on the assumption of a *c*-axis dimension three times that of $ZrSe_2$. This suggests a new stacking sequence of the selenium lattice rather than a superlattice due to the regular interpolation of additional metal atoms in the $ZrSe_2$ structure. Hf_2Se_3 also gave many additional lines suggesting a superlattice of the *C6* structure, but could not be satisfactorily indexed.

(*d*) *The Monochalcogenides*

TiS, TiSe, and TiTe had all previously been assigned the *B8* structure (Ehrlich 1949; Hägg and Schönberg 1954) but our preparations yielded many more lines than were satisfied by this assumption. Single crystals of TiS were examined by Hahn and Harder (1956) and they derived a structure in which the *B8* arrangement was modified by regular stacking disorders. Our powder data indexed satisfactorily on their unit cell. We found one additional phase of low symmetry with the approximate formula $TiS_{1.2}$. Recently, Hahn and Ness (1957*b*) reported a new determination of the unit cell for both TiSe and TiTe with *a* and *c* dimensions double those of Ehrlich (1949). This is in good agreement with the present findings. The disparity between the observed and calculated densities for these two phases, noted in Table 4, suggests that 10 per cent. of both metal and non-metal positions are empty, but in view of the highly

reactive nature of these substances, the densities may not be very reliable. ZrS was reported by Hägg and Schönberg (1954) as having the tetragonal *B11* structure. We found evidence only for a cubic form which, like "Zr_2S_3", is based upon the NaCl-type lattice and with a quarter of each of the lattice components missing. Several diffraction lines in addition to those reported by Hahn *et al.* (1957) were recorded, requiring a unit cell size twice their value. It is probable that this corresponds to the ordering of the empty sites.

Despite numerous heat treatments, compositions designed to yield ZrSe gave mixtures of unreacted metal and a phase resembling $ZrSe_2$ rather than Zr_2Se_3 which might have been expected. ZrTe on the other hand had the *B8* structure in agreement with Hahn and Ness (1957*a*).

The diffraction pattern of HfS was quite different from that of ZrS and whilst orthorhombic indices could be assigned both to it and to HfSe we have preferred not to quote the unit cells from which they were derived, uncertain as we are of their reliability.

(*e*) *Stoichiometry*

A number of the phases we prepared had been previously described in the literature as variable in composition, and it has been customary to assign to them decimal formulae based on chemical analytical results. Biltz, Ehrlich, and Meisel (1937) gave the formula of their titanium trisulphide as $TiS_{2\cdot96}$, and Strotzer, Biltz, and Meisel (1940) consistently quote n values in ZrS_n to three places of decimals, their zirconium trisulphide, for example, being given the formula $ZrS_{2\cdot912}$.

It is recognized among analysts that sulphur determinations by methods involving roasting in air or oxygen and the subsequent estimation of the SO_2 are by no means reliable. The main difficulty is to free the metal oxide from the last traces of sulphur. Such a technique was the one largely adopted by Biltz and his coworkers, and it is a matter for surprise to find formulae quoted to a degree of accuracy which neither the method nor the results of their analyses could justify. An error of 0·1 per cent. in the analysis of both components in TiS_3—which may be expected even when using the most refined techniques—can lead to extremes of formula $TiS_{2\cdot984}$ and $TiS_{3\cdot016}$. When coupled with the impurities present in the metals an even greater degree of uncertainty in the formula must be recognized. There is little chemical evidence to suggest that the trichalcogenides are anything but stoichiometric.

In between the limits AX_2 and AX gross changes of chemical composition in a particular phase may occur which are well outside the limits of experimental error. All the dichalcogenides have a range of composition extending from AX_2 to at least $AX_{1\cdot7}$.

Most striking, perhaps, of the non-stoichiometric systems yet described, is the phase varying in composition from Zr_5S_8 to Zr_9S_8. Many of the supposedly simple oxides with the NaCl structure such as NbO, TiO and VO (reported respectively by Andersson and Magnéli 1957; Ehrlich 1939; Schönberg 1954) have a quarter of both metal and non-metal sites vacant. ZrS, on our evidence,

presents an exact analogy, and the extended composition range is apparently due to the variation in the number of these sites which are occupied.

It is a matter of considerable doubt whether AX compounds with the *B8* structure can have a range of composition. Before finality may be reached on any particular system detailed studies of the methods of preparation and thermal history should be made and even the introduction of an order-disorder parameter should be considered.

(*f*) *Hafnium and Zirconium Chalcogenides*

In view of the very close similarity between hafnium and zirconium throughout their known chemical behaviour, it is a matter of considerable interest that the chalcogenides of these two elements may differ widely. Hafnium does not form a tri- or a ditelluride although zirconium forms both. Also the sesquisulphides and sesquiselenides of the two metals differ in structure. While in the case of the sesquiselenides the differences may simply be due to stacking imperfections, for the sesquisulphides, the differences are profound, not only in structure but also in appearance. This is a matter for further study.

IV. Acknowledgments

The authors wish to express their thanks to Dr. B. Dawson for helpful discussions, and in particular for those concerning the data for the AX_3 compounds which led to the realization that twinning had occurred. They also wish to thank Miss Joy Bear for carrying out the density determinations and a number of the analyses.

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THE SULPHIDES, SELENIDES, AND TELLURIDES OF TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM

II. CHEMICAL PROPERTIES

By Joy Bear* and F. K. McTaggart*

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Summary

Reactions of the main phases (AX_n where $n \geqslant 1$) occurring in the 12 systems comprising the sulphides, selenides, and tellurides of Ti, Zr, Hf, and Th are discussed. These reactions include those with oxygen, chlorine, alkali metals, sulphur, and selenium, acids, alkalis, oxidizing agents, alcohols, hydrogen, and thermal degradation in a vacuum. A number of heats of formation are given.

I. Introduction

Recently a re-examination of the systems Ti-S, Ti-Se, Ti-Te, and Zr-S was made by McTaggart and Wadsley (1958), who also investigated the previously undescribed systems Zr-Se,† Zr-Te,† Hf-S, Hf-Se, Hf-Te. In addition, McTaggart (unpublished data) has re-examined the systems Th-S, Th-Se, Th-Te, and it is believed that between the limits $AX_{1 \cdot 0}$—$AX_{\max.}$ the main phases occurring in the 12 chalcogenide systems have now been identified.

Previous workers concerned themselves almost entirely with the phases present, and only to a limited extent with problems such as the extent of phase regions, variations in molecular volumes, and crystal structures. In a few cases data were given on the reactions of the compounds with certain acids (usually HCl, H_2SO_4, and HNO_3), alkalis, H_2O_2, and bromine water, but this was scarcely more than a side issue. In addition to this, over the past few years there have been isolated reports on certain reactions of several sulphides, mainly of titanium, such as the reduction with alkali and alkali earth metals of TiS_2 to titanium metal, the reaction of TiS_2 with alcohol, and the reaction of TiS_2 with BaS, etc. to form compounds of the sulphospinel type, e.g. $BaTiS_3$. There have also been reports on the reduction of the sulphides of titanium and thorium by means of hydrogen.

However, in all, the chemical reactions of this large group of compounds were almost unknown. Using the materials synthesized for the studies on the 12 systems described by McTaggart and Wadsley, an effort has been made to elucidate some of the chemical behaviour of these chalcogenides and to place their

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† During the writing of this paper two notes by Hahn and Ness (1957*a*, 1957*b*) appeared on the Zr-Se and Zr-Te systems. Their data are in agreement with ours so far as the phases present are concerned.

chemistry on a more systematic basis. The work of the above authors should be referred to for descriptions of the preparation of the compounds, the structures of the phases present, and the appearance and density of each phase.

In the present paper some results obtained are at variance with previously reported reactions. These differences may be ascribed, firstly, to the fact that earlier workers frequently used materials containing relatively large amounts of impurities; secondly, to their failure to realize that surface oxidation of the chalcogenides is often rapid and in such cases protective layers are formed; and thirdly, to their failure to identify accurately the products of reaction, for example, a residue of tellurium was often assumed to be unattacked chalcogenide.

With the object of avoiding these possible sources of error, all our chalcogenides were prepared from highly pure materials and they were all stored and manipulated in an atmosphere of dry argon.

II. Methods of Preparation

It may not be out of place at this point to mention methods that have been proposed for the preparation of these chalcogenides, other than direct synthesis from the elements. This becomes a discussion of methods for sulphides only as there are no data in the literature on the preparation of selenides and tellurides other than by direct reactions.

Montigne (1947) claimed that Th_3Te was formed by reducing $ThTeO_4.8H_2O$ with hydrogen at 400 °C, but we have not been concerned with phases lower than AX.

(i) Disulphides may be synthesized by reacting the anhydrous metal chlorides with H_2S at a red heat

$$ACl_4+2H_2S\rightarrow AS_2+4HCl.$$

This method is satisfactory and is capable of producing disulphides of high purity provided precautions are taken to remove or prevent contamination due to chlorides. It would probably be the most favourable method for production of large quantities.

(ii) Oxides will react under some conditions to yield sulphides. Thus Schwartz and Koster (1956) produced a titanium sulphide containing 46 to 48 per cent. Ti and 52 to 54 per cent. S (a mixture of Ti_2S_3 and TiS_2 phases) from TiO_2, H_2S, and CS_2 at 900 to 1000 °C. Eastman *et al.* (1950) formed ThS_2 from ThO_2, H_2S, and C. Instead of H_2S, solid sulphides such as ZnS and FeS have been used (Kleffner 1934), thus:

$$ZnS+TiO_2+C\rightarrow TiS_2 \quad \text{commencing at 1200 °C,}$$
$$FeS+TiO_2+C\rightarrow TiS_2 \quad \text{rapidly at 1500 °C.}$$

(iii) Instead of reacting metals with sulphur, metal hydrides may be used. Also, metals or metal hydrides may be reacted with H_2S instead of sulphur, for example, Eastman *et al.* (1950) found that the reaction between ThH_4 and H_2S could be controlled to yield any desired sulphide.

(iv) Having obtained disulphides, higher sulphides such as the AS_3 type may be formed by heating the former with sulphur in evacuated vessels. Some

lower sulphides may be formed by degradation ; others by reacting the disulphides with metal.

Of the above methods, (iv) applies equally well to selenides and tellurides and it is likely that (iii) does also.

However, it has been concluded that for the preparation of chalcogenides of high purity for research purposes the direct synthesis from the elements is to be preferred.

III. Heats of Formation

Very few data are available on the heats of formation of these chalcogenide compounds. Eastman *et al.* (1950) quoted a value of 131 kcal for Th_2S_3, the result of direct measurement ; but their other values for their thorium sulphides were calculated. The difficulties encountered in determining heats of combustion of this class of compound in a bomb calorimeter are considerable. It is often impossible to burn all the sample even in the presence of combustible material, and some of the higher compounds, especially tellurides, lose chalcogen by degradation and volatilization during burning, the latter subliming onto the walls of the bomb. In the cases of sulphur and sulphides the formation of SO_3 as well as SO_2 and the formation of sulphuric acid, if any moisture is present, can lead to large errors. These effects are well recognized (see, for example, Hubbard, Katz, and Waddington 1954). It was apparent from our work that similar problems are encountered with selenium and tellurium and their compounds.

Sulphur itself, under the conditions obtaining in the bomb as a result of the systematized procedure of drying, sweeping with oxygen, pressure adjustment, etc. yielded a consistent heat of combustion of 74·5 kcal. This may be compared to $\Delta Hf^0 = 69{\cdot}3$ (g) and 75·2 (liq.) accepted in the literature (for example, Handbook of Chemistry and Physics 1954–55) as the heats of formation of SO_2. Similarly, selenium and tellurium when ignited with sulphur as the combustion aid, consistently yielded 70 and 108 kcal respectively (compare $\Delta Hf^0 = 56{\cdot}4$ and 78·3 kcal found in the literature). The values found by experiment were used in our calculations. Indeed, the use of the quoted value for TeO_2 led to the improbable result of a negative heat of formation for all the tellurides. The following heats of formation (kcal/g-mol) were also used in our calculations: TiO_2 226 (Humphrey 1951), ZrO_2 261·5 (Humphrey 1954), HfO_2 266 (Humphrey 1953), and ThO_2 293 (Huber, Holley, and Meierkord 1952).

After a number of determinations involving most of the compounds at our disposal we derived only two series of values which are sufficiently accurate and reproducible to warrant discussion. These were obtained using sulphur as a combustion aid, and are listed in Table 1.

The diminution in affinity between the metals and the chalcogens as one proceeds from sulphur to tellurium is evident. As the $ThX_{1\cdot5}$ compounds all have greater heats of formation than the TiX_2 compounds, in spite of their lower chalcogen content, it is evident also that there is an increase in affinity between metal and a given chalcogen as one goes from titanium to thorium. This may be compared to the increasing values shown in the series of dioxides.

We were unable to distinguish between the heats of formation of the pairs of compounds TiS_3 and TiS_2, $ThS_{2\cdot5}$ and ThS_2, these being the only pairs that behaved satisfactorily in the bomb. This is in agreement with Biltz and Ehrlich (1937) and Strotzer, Biltz, and Meisel (1939), who calculated from vapour pressure data that there could be only small differences in the heats of formation of the tri- and disulphides of titanium and zirconium.

$$TiS_{2(solid)}+S_{(rhomb)}=TiS_3+4 \text{ kcal (degradation above 500 °C)},$$
$$ZrS_{2(solid)}+S_{(rhomb)}=ZrS_3+8\cdot5 \text{ kcal (degradation above 700 °C)}.$$

Similar considerations should apply to all the tri- (or $AX_{2\cdot5}$) compounds of this group as they all degrade readily on heating in vacuum. Degradation is discussed in Section IV.

TABLE 1

HEATS OF FORMATION OF CHALCOGENIDES

Compound	TiS_2	$ThS_{1\cdot5}$	$TiSe_2$	$ThSe_{1\cdot5}$	$TiTe_2$	$ThTe_{1\cdot5}$
Heats of formation (kcal/g-mol)	102	119	97	112	55	75

IV. THERMAL STABILITY

Normally when $AX_{max.}$ compounds are synthesized by direct reaction of the elements, they are freed from excess chalcogen by heating the chalcogenide end of the synthesis tube to 350 °C in the case of sulphides, 450 °C for selenides, and 550 °C for tellurides, with the other end at or below room temperature. Under these conditions excess chalcogen sublimes off. The $AX_{max.}$ compounds so obtained are listed in Table 2, the second column of which gives the n values to the nearest 0·05 as determined by analysis. The manner in which the various compounds degrade when heated in vacuum is shown by reference to the third column, in which formulae are given of the chalcogenides resulting from heating to approximately 950 °C in the manner described above. It will be seen that dichalcogenide phases result in every case from the degradation of the tri-, or $n=2\cdot5$ compounds. The diselenide and ditelluride of titanium degrade without change of phase, as for these compounds the region $TiX_{1\cdot0}$ to $TiX_{2\cdot0}$ may be regarded as a single phase.

Two tendencies are evident:

(i) The stability of the compounds increased from titanium, through zirconium and hafnium, which are closely similar, to thorium.

(ii) The stability decreases, for each Group IV metal, as one goes from sulphide, through selenide, to telluride.

Both these trends are in keeping with other known properties of the metals and the chalcogens and confirm the increasingly saltlike character of the compounds of thorium, compared with the preceding Group IV elements on the one hand, and the more metallic nature of tellurium, which tends to form alloylike compounds, on the other.

Temperatures higher than those indicated in Table 2 were not used. Eastman *et al.* (1950) have claimed that ThS_2 is stable to its melting point (about 1900 °C) but loses some sulphur above this temperature. D'Eye, Sellman, and Murray (1952) stated that $ThSe_{2\cdot0}$ degrades to $ThSe_{1\cdot7}$ above 1000 °C. We were, however, unable to confirm the statement of D'Eye and Sellmann (1954) that $ThTe_2$ (and indeed all lower thorium tellurides also) decompose above 500 °C, eventually forming the elements. Our $ThTe_2$ and $ThTe_{1\cdot0}$ were stable at 950 °C. It is likely that the high oxygen content of D'Eye's materials, which gave rise to oxy compounds such as ThOTe, was the cause of the decomposition. The reaction $2ThOTe \rightarrow ThO_2 + 2Te + Th$ proceeds readily, and if the tellurium is sublimed off, as is the case in the type of degradation under discussion, the ThO_2 would react with the telluride present, thus eventually causing complete decomposition.

TABLE 2

THERMAL STABILITY AND HYDROGEN REDUCTION DATA FOR CHALCOGENIDES

Compound	Formula after Removal of Excess Chalcogen	Degraded at °C in a Vacuum	Dichalcogenide after Hydrogen Reduction at 950 °C
TiS_3	$TiS_{2\cdot95}$	900° $TiS_{1\cdot65}$	$TiS_{1\cdot25}$
$TiSe_2$	$TiSe_{2\cdot0}$	950° $TiSe_{1\cdot7}$	$TiSe_{1\cdot4}$
$TiTe_2$	$TiTe_{2\cdot0}$	950° $TiTe_{1\cdot55}$	$TiTe_{1\cdot45}$
ZrS_3	$ZrS_{2\cdot95}$	950° $ZrS_{1\cdot9}$	$ZrS_{1\cdot4}$
$ZrSe_3$	$ZrSe_{2\cdot95}$	950° $ZrSe_{1\cdot9}$	$ZrSe_{1\cdot7}$
$ZrTe_3$	$ZrTe_{2\cdot9}$	950° $ZrTe_{1\cdot7}$	$ZrTe_{1\cdot7}$
HfS_3	$HfS_{2\cdot0}$	940° $HfS_{1\cdot95}$	$HfS_{1\cdot5}$
$HfSe_3$	$HfSe_{2\cdot9}$	940° $HfSe_{1\cdot85}$	$HfSe_{1\cdot75}$
Hf_2Te_3	$HfTe_{1\cdot5}$	940° $HfTe_{1\cdot2}$	$HfTe_{1\cdot1}$
$ThS_{2\cdot5}$	$ThS_{2\cdot5}$	950° $ThS_{2\cdot0}$	$ThS_{2\cdot0}$
$ThSe_{2\cdot5}$	$ThSe_{2\cdot5}$	950° $ThSe_{2\cdot0}$	$ThSe_{2\cdot0}$
$ThTe_{2\cdot5}$	$ThTe_{2\cdot5}$*	950° $ThTe_{1\cdot95}$	$ThTe_{1\cdot9}$

* Removal of excess Te in this case required special care (McTaggart, unpublished data).

The fact that all the higher chalcogenides (i.e. AX_3 and $AX_{2\cdot5}$ types) lose part of their sulphur, selenium, or tellurium, when heated in a vacuum has been used by several of the earlier workers to determine the compositional upper limits of certain phases, notably the dichalcogenide phases. This so-called " tension analysis " depends on the fact that for a given chalcogenide at a given temperature there is a certain vapour pressure of chalcogen above the compound. This chalcogen is gradually condensed off and a series of vapour pressure values is obtained corresponding to different compositions of the solid chalcogenide. Curves, one for each temperature, may be drawn by plotting vapour pressures against n values in the chalcogenide formula AX_n. Each curve will intersect the composition axis when the vapour pressure value is zero. Such curves are useful for determining the minimum temperature necessary to bring about degradation of a compound and may give information on the extent of a phase

region. However, with the advent of better X-ray techniques and an improvement in the interpretation of X-ray patterns, this rather laborious technique has been found to be less useful for this group of compounds than was first thought. Further use may be found for the technique in the elucidation of the nature of the bonding present in certain chalcogenides which take up large excesses (50 per cent. upwards) of chalcogen without significant change in their general appearance and without the formation of another phase. Such "excess" chalcogen may be sublimed off fairly readily but requires a higher temperature to produce a given vapour pressure than is necessary for free chalcogen. The Th-Te system provides an example of this and it is hoped to report in more detail on this and other similar systems in a subsequent paper.

V. Hydrogen Reduction

All the dichalcogenides were reduced in highly purified hydrogen for 3 hr at 950 °C. The compositions of the resulting materials are given in column four of Table 2. It will be seen that once again there is a marked difference in the stabilities, the titanium compounds being again the least stable and the thorium compounds the most stable. TiS_2, for example, reduces to $TiS_{1\cdot25}$, while ThS_2 is not reduced at all. Between these two extremes, zirconium and hafnium compounds exhibit intermediate stability and resemble one another closely, except for hafnium telluride, which is exceptional throughout. Under the conditions of hydrogen reduction the tellurides are more stable than the corresponding selenides, and selenides are more stable than sulphides. None of the thorium compounds appears to undergo appreciable reduction.

Schwartz and Koster (1956) have shown that, at 1100 °C, hydrogen reduces TiS_2 to $TiS_{1\cdot0}$. This is in agreement with our findings. No evidence could be obtained to suggest that hydrogen entered the chalcogenide lattice during reduction. Analysis of the compounds for hydrogen before and after the reductions yielded results that did not differ significantly.

VI. Reduction with Metals

(*a*) *Alkali and Alkaline Earth Metals*

The alkali metals reduce all the sulphides, selenides, and tellurides, regardless of composition, to the Group IV metal. This fact has been used as a basis for the analyses of this class of compound as described previously.

If less than the theoretical amount of Na or K is used, compounds may be formed by reactions typified by the following:

$$TiS_3 + Na \rightarrow NaTiS_3.$$

Schwartz and Koster (1956) found that Al, Ca, and CaH_2 all reduced titanium sulphides to the metal, while Mg in argon at 1000 °C produced 98–99 per cent. of titanium metal.

Hahn and Harder (1956) have prepared $CuTi_2S_4$, which has a spinel structure, from Cu_2S, TiS_2, and S, and Hahn and Mutschke (1956) have prepared thioperovskites such as $SrTiS_3$, $BaTiS_3$, and $BaZrS_3$ from TiS_2 (or ZrS_2) and the appropriate alkaline earth sulphide. The properties of these latter compounds are stated to

be akin to those of the alkaline earth sulphides themselves. It appears likely that a wide range of compounds may be produced by this type of reaction forming a series analogous to the titanates.

(b) Reaction with Other Subgroup IV Metals

The technique of forming a lower chalcogenide by heating together a higher one and the metal in the correct proportions, for example,

$$ZrS_3+Zr\rightarrow Zr_2S_3,$$
$$ZrS_2+Zr\rightarrow 2ZrS,$$

was used to some extent by earlier workers. These reactions are quite general and form a useful basis for the preparation of compounds of a wide range of composition when the necessary higher chalcogenide has been prepared.

As the thorium compounds are more stable than those of the other elements it was of interest to determine to what extent thorium would reduce compounds of the other elements and vice versa. The sulphides ThS_2 and TiS_2 were chosen for experiments. ThS_2 was intimately mixed with titanium powder and TiS_2 with thorium powder. The mixtures were sealed under vacuum in silica tubes and heated to 800 °C for several days.

X-Ray analysis then showed that for ThS_2+Ti the ThS_2 had been reduced to approximately $ThS_{1\cdot5}$ and that there was still a trace of free titanium metal. However, in the reaction between TiS_2 and Th the product consisted mainly of a thorium sulphide of composition about $ThS_{1\cdot5}$ and a subsulphide of titanium ($TiS_{<1\cdot0}$) of undetermined composition. These results are in keeping with the stabilities of the Ti-S and Th-S systems and confirm that thorium exerts a greater affinity towards sulphur than does titanium.

VII. Reactions with Sulphur and Selenium

It has been established that a higher chalcogenide may be formed from a lower compound by the direct reaction of the lower compound with the appropriate chalcogen, for example,

$$TiS+S\rightarrow TiS_2,$$
$$Zr_2S_3+3S\rightarrow 2ZrS_3, \text{ etc.}$$

These reactions are generally applicable and have been used at times in the synthesis of certain phases.

Our experimental work has shown that sulphur will displace both selenium and tellurium quantitatively from selenides and tellurides, and that selenium will displace tellurium from tellurides. The following are a few examples of what also appears to be a general type of reaction:

$$ZrTe_3+3S\rightarrow ZrS_3+3Te, \qquad TiTe_2+2S\rightarrow TiS_2+2Te,$$
$$ZrTe_3+2S\rightarrow ZrS_2+3Te, \qquad TiTe_2+2Se\rightarrow TiSe_2+2Te,$$
$$ZrTe_3+3Se\rightarrow ZrSe_3+3Te, \qquad ZrSe_3+3S\rightarrow ZrS_3+3Se,$$
$$ZrTe_3+2Se\rightarrow ZrSe_2+3Te, \qquad TiSe_2+3S\rightarrow TiS_3+2Se,$$
$$TiTe_2+3S\rightarrow TiS_3+2Te, \qquad TiSe_2+2S\rightarrow TiS_2+2Se.$$

These reactions may be carried out by sealing the chalcogenide and chalcogen in a silica tube, after evacuation, and heating homogeneously to 600–700 °C

for some time. At the completion of the reaction the free chalcogen is sublimed off to the other end of the tube under the appropriate conditions as discussed under the synthesis of chalcogenides. An exception to the above temperature range must be made if TiS_3 is the desired product, as TiS_3 will not be formed if the temperature exceeds about 550 °C.

If less than the stoicheiometric quantities of chalcogen are used, a part of the chalcogenide will be completely reacted and the remainder may be left unchanged. Thus if one-half of the theoretical quantity is used, the following type of reaction results:

$$2ZrTe_2+2S \rightarrow ZrS_2+ZrTe_2+2Te,$$
$$2ZrTe_2+2Se \rightarrow ZrSe_2+ZrTe_2+2Te,$$
$$2TiTe_2+2S \rightarrow TiS_2+TiTe_2+2Te,$$
$$2TiSe_2+2S \rightarrow TiS_2+TiSe_2+2Se,$$
$$2TiTe_2+2Se \rightarrow TiSe_2+TiTe_2+2Te.$$

However, if the initial chalcogenide itself suffers degradation at the reaction temperature the following type of reaction will occur:

$$2ZrTe_3+2S \rightarrow ZrS_2+ZrTe_2+4Te,$$
$$2ZrTe_3+2Se \rightarrow ZrSe_2+ZrTe_2+4Te,$$
$$2ZrSe_3+2S \rightarrow ZrS_2+ZrSe_2+4Se.$$

There is no evidence to suggest the formation of mixed chalcogenides containing two chalcogens: *A*SSe, *A*STe, etc.

VIII. Reactions between Chalcogenides

It may be inferred from the above reactions that many interactions between the chalcogenides are possible. This has been found to be so. Two examples show the type of reaction that may be expected:

$$2ZrSe_3+ZrTe_3 \rightarrow 3ZrSe_2+3Te,$$
$$TiS_2+ThTe_2 \rightarrow ThS_2+TiTe_2.$$

IX. Oxidation

It has already been noted that many of the chalcogenides undergo oxidation in the air. This varies from slight surface oxidation to inflammability and it was because of these effects that it became our practice to open, store, and manipulate all samples in dry argon. Even the compounds that show no visible change were found to undergo slow oxidation. For example, TiS_3, which when freshly prepared had a sulphur content of 66·3 per cent., after storage in air for some months was found to contain 65·4 per cent. sulphur, and on chlorination left a small residue of TiO_2, whereas TiS_3 stored in argon neither changed its sulphur content nor left any visible residue of TiO_2 on chlorination. ZrS_2 absorbed oxygen rapidly, as described by McTaggart (1958), the quantity amounting to 0·25 per cent. after a few days. In this case, a protective layer apparently formed so that the rate of absorption slowed to almost zero. Several of the compounds and notably the monotellurides of titanium and zirconium, were spontaneously inflammable when opened in air (compare Zr powder), but when first opened in argon and subsequently allowed slow access to air they oxidized only slowly and to a limited extent.

An attempt was made to measure and compare rates of oxidation for a number of the chalcogenides of titanium and zirconium at 150 and 300 °C in air. This was not very successful, probably due to the samples having different particle size, crystal structure, etc. However, it appeared that tellurides tend to be more resistant to oxidation than selenides and sulphides (see Table 3), although this is not always so at the lower temperature. The higher chalcogenides tend to be slightly more resistant than the lower ones (see the right-hand section of Table 3), although there are apparent exceptions to this.

TABLE 3

OXIDATION OF CHALCOGENIDES IN AIR

Compound	Percentage Sample Oxidized at:			Compound	Percentage Sample Oxidized at:		
	150 °C for 10 Days	300 °C for 1 Day	300 °C for 3 Days		150 °C for 10 Days	300 °C for 1 Day	300 °C for 3 Days
$TiTe_2$	3	8	15	$ZrSe_3$	20	35	70
$TiSe_2$	15	—	70	$ZrSe_2$	25	25	70
TiS_2	35	87	100	$ZrSe_{1\cdot0}$	25	100	100
$ZrTe_3$	—	25	37	$ZrTe_3$	—	25	37
$ZrSe_2$	20	35	70	$ZrTe_2$	33	38	45
ZrS_3	3	40	100	$ZrTe_{1\cdot0}$	40	45	63
$ZrTe_2$	7	38	45				
$ZrSe_2$	25	25	70				
ZrS_2	4	53	60				

All the chalcogenides, when heated in air or oxygen, ultimately yield the metal oxide and the oxide of the chalcogen associated with them, namely, SO_2, SeO_2, or TeO_2. The protective layer of oxide which forms on the surface of the compounds of zirconium, hafnium, and thorium undoubtedly slows the rate of oxidation and frequently makes it appear that oxidation has ceased at between 40 and 60 per cent. Also, the formation of TeO_2 may provide some protection for the tellurides. The presence of an oxide film has probably been responsible for a number of incorrect properties being attributed to those compounds that have been investigated previously.

X. REACTIONS WITH CHLORINE

The chalcogenides all react readily with chlorine below 300 °C, the reaction in some cases commencing at room temperature. The products consist of the tetrachloride of the Group IV metal together with the chloride of the chalcogen. The following are typical reactions:

$$TiS_3+5Cl_2\rightarrow TiCl_4+3SCl_2,$$
$$HfSe_3+8Cl_2\rightarrow HfCl_4+3SeCl_4,$$
$$ZrTe_3+8Cl_2\rightarrow ZrCl_4+3TeCl_4.$$

These reactions all proceed to completion on moderate heating. In many of them the products may be separated by a simple type of fractional condensation, but SCl_2+TiCl_4, for example, form an addition compound—a yellow solid.

If the sample of chalcogenide has undergone partial oxidation some metal oxide remains.

XI. Reactions with Acids, Alkalis, etc.

In the discussion of these reactions the compounds $ThX_{2\cdot5}$ are treated as if they were AX_3 compounds. It may also be remarked that difficulties due to the formation of protective layers of insoluble materials on the surfaces of the chalcogenides sometimes arose and attempts were made to overcome these by vigorous stirring and breaking up of the samples and by allowing ample time for observations on the reactions. If the results were ambiguous, both quantitative and qualitative analyses were done on solutions and solid materials in order to determine what change had occurred.

(*a*) *Water*

None of the compounds appeared to react with water, either at room temperature or at the boiling point, although on boiling, most of the sulphides and selenides gave traces of H_2S or H_2Se and the tellurides often imparted to the water a pale mauve colour. However, as certain AX_3 and AX_2 compounds react with alcohols to form esters (see below), in these circumstances the esters being soluble in the alcohols, it must be assumed that reaction with water does occur, at least with the same compounds, but that insoluble hydroxide products are formed which protect the chalcogenides from further attack.

(*b*) *Oxidizing Agents*

(i) *Concentrated HNO_3.*—Cold concentrated HNO_3 reacts without exception with the compounds. The reaction is vigorous for the AX_3 and AX_2 chalcogenides and usually explosive and accompanied by flashes of light with the A_2X_3 and lower types. Brown fumes are evolved and some white to grey residue, an oxide material, is left in a yellow to green solution. The bulk of the metal is found in the acid solution, together with the chalcogens, although SO_2, SeO_2, etc. may be evolved during the action.

(ii) *50 Volume H_2O_2.*—All AS_3, AS_2, ASe_3, and ASe_2 compounds, except those of thorium, react at room temperature to yield white insoluble residues. Boiling the peroxide causes accelerated action and the thorium compounds ($ThS_{2\cdot5}$, $ThSe_{2\cdot5}$, and $ThTe_{2\cdot5}$ and the di-compounds) also react. All these reactions go to completion on boiling. Most of the lower chalcogenides do not react at room temperature, and only slowly and partially at the boiling point. However, $TiS_{1\cdot5}$, $TiS_{1\cdot0}$, $TiSe_{1\cdot0}$, $ZrSe_{1\cdot5}$, $ZrSe_{1\cdot0}$, $ZrTe_{1\cdot0}$, and $HfS_{1\cdot5}$ react completely on boiling. For all types of sulphides and selenides the stability increases from titanium to thorium. The higher tellurides are markedly more stable than the corresponding sulphides and selenides, for example, $TiTe_3$ and $ZrTe_3$ do not react under any conditions, but the lower tellurides of all four elements react slowly at the boiling point and there is little sign of increased stability here as one goes from titanium to thorium.

(*c*) *Concentrated* H_2SO_4

Cold concentrated sulphuric acid reacts completely with ZrS_2, HfS_2, and ThS_2 giving H_2S and depositing a thick white precipitate. $ZrS_{1\cdot5}$, $ZrS_{1\cdot0}$, $HfS_{1\cdot5}$, and $HfS_{1\cdot0}$ react in a similar manner but to a limited extent. None of the other compounds is attacked. On boiling, however, all the chalcogenides are attacked. With the sulphides there is a brisk effervescence of SO_2, some sulphur usually separates, a whitish residue containing metal oxide or sulphate remains and part of the metal is found in solution. With the selenides there is also a brisk effervescence as SeO_2 is evolved; black globules of selenium form and the solution usually clears, but there may be some white or grey flocculent residue. The metals are found to be almost wholly in the acid solution. From the tellurides there is also vigorous effervescence and a strong smell resembling SO_2. A deep purple colouration develops, then fades, but the solution usually remains milky. On cooling, masses of fine crystals of tellurium separate and the metals are found to be almost wholly in solution.

(*d*) *Concentrated HCl*

At room temperature the only chalcogenides found to react are the thorium tellurides, all of which give a steady effervescence; tellurium separates and the thorium is found in the solution. Some of the sulphides, namely, ZrS_2, HfS_2, $ThS_{1\cdot5}$, and $ThS_{1\cdot0}$, yield some H_2S but the reactions do not proceed far. Some of the selenides behave similarly.

On boiling, the following sulphides appear to be non-reactive: TiS_3, TiS_2, ZrS_3, HfS_3, and $ThS_{2\cdot5}$. However, ZrS_2, HfS_2, and ThS_2 dissolve completely with the evolution of H_2S, the metals going into solution. The remaining lower sulphides suffer only partial attack ranging from negligible for those of titanium to almost complete for those of thorium.

The selenides are, in general, more reactive than the sulphides. Thus the higher compounds, unlike the corresponding sulphides, suffer slight attack and $TiSe_2$ dissolves completely. However, the other diselenides are not attacked to any great extent.

The tellurides all react completely, usually with no evolution of gas. Metallic tellurium is precipitated and this is often difficult to distinguish in appearance from the original chalcogenide. Probably for this reason earlier workers reported that there was no reaction between $TiTe_2$ and $TiTe_{1\cdot0}$ and boiling HCl.

(*e*) 2N H_2SO_4

This acid may be taken as representing dilute mineral acids in its action on the chalcogenides.

In the cold, slow steady reactions with effervescence of H_2S are found for ZrS_2, HfS_2, ThS_2, and $ThS_{1\cdot5}$ but not for TiS_2. The AS_3 type of sulphides does not react at all and the other lower sulphides yield some H_2S while being slowly attacked. The selenides are non-reactive except for the $ASe_{1\cdot5}$ and ASe compounds of Hf and Th which evolve some H_2Se. These show decreasing stability from titanium to thorium, the $ThSe_{1\cdot5}$ and $ThSe_{1\cdot0}$ compounds reacting almost completely. Except for $TiTe_2$, the tellurides all react slowly.

On boiling, the AS_3 compounds are still found to be stable. The AS_2 compounds range from TiS_2, which is the most stable and gives only a slow incomplete reaction, to ThS_2 which dissolves rapidly and completely with evolution of H_2S and precipitation of white, hydrated thorium sulphate. The lower sulphides are more reactive than the AS_2 type and the same trend is found from titanium to thorium.

The selenides behave similarly to the sulphides throughout, the diselenides being somewhat less reactive than the disulphides.

With regard to the tellurides, there is no action for $TiTe_2$ and only a very slow one for $ZrTe_3$. All the others go to completion, the reactions being more vigorous as the tellurium content decreases and also as one goes from titanium to thorium.

(*f*) *5N NaOH Solution*

The AS_3 and AS_2 compounds of titanium, zirconium, and hafnium react readily and to completion in boiling NaOH to yield white flocculent residues and bright yellow solutions. The lower sulphides of these three metals react slowly and partially, becoming somewhat flocculent, but otherwise not changing in appearance. The two higher sulphides of thorium do not react, nor do the lower ones. Although these become flocculent, no chemical evidence for reaction is found.

The selenides all react to give dark red to red-brown solutions and white residues. On cooling, selenium separates as a layer of crystals on top of the solution.

The tellurides react even more readily than the selenides, yielding darker residues and crystalline masses of tellurium on cooling.

(*g*) *Discussion of Wet-Way Reactions*

Except for TiS_2, the disulphides show noticeable saltlike characteristics in that they react readily with strong or dilute mineral acids to form H_2S. TiS_2, which does not behave in this manner, is more typical of the semimetallic sulphides. This is in keeping with the tendency found within the group for the basicity to increase up to thorium. As thorium is approached there is a greater likelihood of the metal exerting the normal valency of four and this causes increased stability towards some reagents, e.g. NaOH and H_2O_2.

The higher sulphides, AS_3 and $AS_{2\cdot5}$ types, behave like polysulphides and tend to resist attack by acids but not by oxidizing agents, while the lower ones are more metallic. The tellurides are more akin to alloys and the action of certain of the reagents suggests this. In general, the stability of the tellurides decreases towards thorium. The selenides fall between the sulphides and the tellurides, usually resembling the former but sometimes being more like the latter.

XII. Reactions with Alcohols

It has been stated by Boyd (1951) that TiS_2 reacts with alcohols and phenols, under anhydrous conditions, to form esters of orthotitanic acid, and with amines to form amides of the acid. In our work use was made of *n*-butyl alcohol to test

the reactivity of certain chalcogenides. The butyl alcohol was carefully dried and samples were refluxed with it, under anhydrous conditions, for periods of several days. The evolution of H_2S and H_2Se was detected by lead acetate papers placed at the top of the drying tube on the reflux condenser, and the residues were analysed both chemically and by X-ray diffraction.

(i) Sulphides: TiS_2 reacted readily with the evolution of H_2S:

$$TiS_2 + 4C_4H_9OH \rightarrow (C_4H_9O)_4Ti + 2H_2S.$$

ZrS_2 reacted less rapidly and HfS_2 gave a small amount of H_2S initially, but the reaction did not proceed. ThS_2 did not react at all.

The trisulphides TiS_3 and ZrS_3 also reacted, the latter only slowly to deposit sulphur:

$$TiS_3 + 4C_4H_9OH \rightarrow (C_4H_9O)_4Ti + 2H_2S + S.$$

(ii) Selenides: $TiSe_2$ reacted readily, yielding H_2Se, and depositing some selenium.

(iii) Tellurides: $TiTe_2$ reacted readily and completely, depositing metallic tellurium. $ZrTe_3$ also reacted fairly readily. $ThTe_2$ appeared to react to a very limited extent only.

In general, it may be said that the chalcogenides of the lower members of the group react readily to yield esters. Those of the higher members less readily, and for thorium there is little tendency for this type of reaction to occur. The tellurides appear to react faster than the sulphides.

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THE SULPHIDES, SELENIDES, AND TELLURIDES OF TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM

III. ELECTRICAL PROPERTIES

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Summary

The resistivities, types of conduction, thermo-e.m.f.'s, and rectifying ability of the sulphides, selenides, and tellurides of the elements Ti, Zr, Hf, and Th were determined. A wide range of properties was found and the variations reflect the trend within this group of compounds from semimetallic in the case of Ti to metallic in the case of Th. The transition from non-metallic to metallic affinities that occurs from sulphur to tellurium is likewise evident.

I. Introduction

Previous investigators of these systems concerned themselves almost entirely with the consideration of phases and phase regions, and to a lesser extent with crystal structure and changes in molecular volumes. There was even much disagreement about the phases present. Some reactions of the materials with acids, alkalis, and oxidizing agents had been noted but nothing appeared to be known concerning the electrical properties of this substantial group of compounds beyond statements by Strotzer, Biltz, and Meisel (1939) and Eastman *et al.* (1950) to the effect that ZrS_3 and ThS_2 seemed to be non-conductors of electricity, and a claim by the latter authors that ThS, Th_2S_3, and Th_7S_{12} had specific resistivities of 10^{-3} to 10^{-4} Ωcm. Many of the investigations had been made with impure materials, especially those involving the thorium chalcogenides, and few of the workers noted that all these materials are subject to at least surface oxidation in the air at room temperatures.

It was decided to investigate the resistivity, type of conduction (metallic, N or P semiconduction), thermoelectric power, and rectifying properties of each of the phases between $AX_{1\cdot0}$ and $AX_{max.}$ now known to exist in the 12 systems comprising the sulphides, selenides, and tellurides of titanium, zirconium, hafnium, and thorium, using the preparations described either by McTaggart and Wadsley (1958), or investigated more recently (McTaggart, unpublished data).

II. Materials

Most of the compounds, namely, the chalcogenides of titanium, zirconium, and hafnium, have already been described in some detail (McTaggart and Wadsley 1958). They are listed in Table 1, which shows the broadly descriptive type

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name (e.g. diselenide etc.), appearance, formula, etc. The thorium compounds are also presented in the same manner. The materials were all finely divided powders, about one-third of which were smooth to the touch and graphitic in nature. In addition to these were single crystals, obtained by sublimation: TiS_3 in the form of ribbons of approximate maximum dimensions 1 cm by 0·25 mm by 0·01 mm; $ZrTe_3$ in the form of needles 0·5 cm by 0·5 mm; $TiTe_2$ in the form of plates 2 by 2 mm.

III. Measurements and Results

(*a*) *Specific Resistivity*

The resistivities of the powders were determined by compressing them between steel plungers in dies of clear plastic material and measuring resistances with either a Thomson bridge (for resistances below 2 Ω) or by direct determination of voltage and current (for resistances above 2 Ω). A pressure equivalent to 25,000 lb/in^2 was chosen; at this pressure the distortion of the plastic die was negligible and the value of resistance measured was no longer subject to rapid change with pressure. The agreement between specific resistivity values so obtained and those found by measurements on single crystals was reasonably good. With TiS_3, for example, where the regular shape of the ribbon-like sublimed crystals permitted their dimensions to be determined very accurately with the aid of a micrometer microscope, the specific resistivity (Sp.K.) of single crystals measuring approximately 0·5 cm by 0·2 mm by 0·008 mm was 2·0 to 2·4 Ωcm, whereas the average value for compressed TiS_3 powder was 6·0 Ωcm. The other single crystals gave even closer agreement with the corresponding compressed powders. Duplicate measurements on a single sample invariably yielded values differing by not more than 10 per cent. and agreement between values obtained from powders representing different syntheses of the same compound was surprisingly good, for example, $TiSe_2$, 0·0020 and 0·0018 Ωcm: $ThTe_{1\cdot0}$, 0·02 and 0·023 Ωcm; $ZrSe_3$, 18,000 and 23,000 Ωcm. Hence, it is considered that the values have a degree of reliability such that conclusions may be drawn from them concerning the nature of the compounds.

The Sp.K. values for the various preparations (Table 1) are shown graphically in Figure 1. The lines joining the points do not necessarily represent intermediate values but are drawn to show the trend in Sp.K. and to enable the eye to follow each metal-chalcogen system.

The main difficulty encountered was the rapid oxidation of several of the preparations. It had been noted in earlier attempts to make measurements on compacts of the materials that the resistance of them increased with time. Some of the compounds, such as $TiTe_{1\cdot0}$ and $ZrTe_{1\cdot0}$, were pyrophoric. In such cases the measurements were carried out in an argon atmosphere.

As an example of the effects of oxidation on the measured Sp.K. value, ZrS_2 may be cited. A fresh preparation of this material, opened and tested in argon, had a Sp.K. of 10 Ωcm. When a portion was left in the air, its Sp.K. rose rapidly as shown in Figure 2, and eventually became relatively steady at about 20,000 Ωcm. Another portion of the material was placed in oxygen at 19·5 °C and the amount of oxygen absorbed was measured. This gave the

TABLE 1

PROPERTIES OF THE CHALCOGENIDES

Material	Formula	Appearance	Specific Resistivity (Ωcm)	Thermo-e.m.f. (mV/°C)	Type of Conduction
Titanium					
Trisulphide ..	$TiS_{2\cdot95}$	Dark blue - black ribbon crystals*	6·0	0·6	N semi
Disulphide ..	$TiS_{1\cdot95}$	Dark bronze*	0·008	0·2	N semi
Sesquisulphide	$TiS_{1\cdot50}$	Black	0·001	—	Metallic
Monosulphide..	$TiS_{1\cdot00}$	Dark grey-brown	0·001	—	Metallic
Subsulphide† ..	$TiS_{0\cdot50}$	Black	0·0003	—	Metallic
Diselenide ..	$TiSe_{2\cdot00}$	Dark purply brown*	0·002	—	Metallic
Sesquiselenide	$TiSe_{1\cdot50}$	Black	0·0005	—	Metallic
Monoselenide	$TiSe_{1\cdot00}$	Black	0·0005	—	Metallic
Subselenide† ..	$TiSe_{0\cdot50}$	Black	0·0002	—	Metallic
Ditelluride ..	$TiTe_{2\cdot00}$	Black*	0·0001	—	Metallic
Sesquitelluride	$TiTe_{1\cdot50}$	Black*	0·0005	—	Metallic
Monotelluride..	$TiTe_{1\cdot00}$	Black*	0·0005	—	Metallic
Subtelluride† ..	$TiTe_{0\cdot50}$	Black, brown tinge	0·0002	—	Metallic
Zirconium					
Trisulphide ..	$ZrS_{2\cdot95}$	Orange*	200,000	1·0	N semi
Disulphide ..	$ZrS_{2\cdot00}$	Brown-violet*	10	0·7	N semi
Sesquisulphide	$ZrS_{1\cdot50}$	Black	0·08	0·05	N semi
Monosulphide..	$ZrS_{1\cdot0}$	Dark grey-black	0·006	—	Metallic
Triselenide ..	$ZrSe_{3\cdot05}$	Black, purple tinge*	20,000	1·0	N semi
Diselenide ..	$ZrSe_{1\cdot95}$	Dark greyish green*	0·10	0·3	N semi
Sesquiselenide	$ZrSe_{1\cdot50}$	Black	0·007	0·05	N semi
Monoselenide	$ZrSe_{1\cdot00}$	Very dark grey	0·004	—	Metallic
Tritelluride ..	$ZrTe_{2\cdot90}$	Black lustrous*	0·0004	—	Metallic
Ditelluride ..	$ZrTe_{1\cdot70}$	Dark purple-brown bronze	0·001	—	Metallic
Sesquitelluride	$ZrTe_{1\cdot50}$	Black	0·0016	—	Metallic
Monotelluride..	$ZrTe_{1\cdot00}$	Black	0·001	—	Metallic
Hafnium					
Trisulphide ..	$HfS_{2\cdot00}$	Bright orange*	100,000M	—	(?) semi
Disulphide ..	$HfS_{2\cdot00}$	Purple-brown	1000M	—	(?) semi
Sesquisulphide	$HfS_{1\cdot50}$	Light yellow-brown	150	0·2	N semi
Monosulphide..	$HfS_{1\cdot00}$	Black	0·50	—	Metallic
Triselenide ..	$HfSe_{2\cdot90}$	Black*	80,000	—0·4	P semi
Diselenide ..	$HfSe_{1\cdot85}$	Very dark brown	20	0·25	N semi
Sesquiselenide	$HfSe_{1\cdot50}$	Black	6	0·2	N semi
Monoselenide	$HfSe_{1\cdot00}$	Black	0·15	—	Metallic
Sesquitelluride	$HfTe_{1\cdot50}$	Black	0·015	—	Metallic
Monotelluride..	$HfTe_{1\cdot00}$	Black	0·004	—	Metallic

* Indicates graphitic materials.

† Not necessarily distinct phases.

TABLE 1 (*Continued*)

Material	Formula	Appearance	Specific Resistivity (Ωcm)	Thermo-e.m.f. (mV/°C)	Type of Conduction
Thorium					
Polysulphide	$ThS_{2\cdot50}$	Light red-brown	5000M	—	(?) semi
Disulphide ..	$ThS_{2\cdot00}$	Brown	10,000M	—	(?) semi
$MX_{1\cdot7}$ type ..	$ThS_{1\cdot70}$	Green-grey	25,000	0·2	N semi
Sesquisulphide	$ThS_{1\cdot50}$	Dark grey	10	0·1	N semi
Monosulphide..	$ThS_{1\cdot00}$	Dark grey	0·2	—	Metallic
Polyselenide ..	$ThSe_{2\cdot50}$	Dark purple	10,000	—0·8	P semi
Diselenide ..	$ThSe_{2\cdot00}$	Dark grey	150,000	—0·5	P semi
$MX_{1\cdot7}$ type ..	$ThSe_{1\cdot70}$	Black	400	0·25	N semi
Sesquiselenide	$ThSe_{1\cdot50}$	Black	4·0	0·1	N semi
Monoselenide	$ThSe_{1\cdot00}$	Black	0·06	—	Metallic
Polytelluride	$ThTe_2$	Black*	4·0	—	N semi
Ditelluride ..	$ThTe_{2\cdot00}$	Black	0·02	—	Metallic
Sesquitelluride	$ThTe_{1\cdot50}$	Black	0·015	—	Metallic
Monotelluride..	$ThTe_{1\cdot00}$	Black	0·02	—	Metallic

* Indicates graphitic materials.

results shown in the second curve in Figure 2. It will be seen that 1·75 c.c. O_2/g ZrS_2 (approx. 0·25 per cent. by weight) was absorbed in 7 days, causing a 2000-fold increase in resistivity. There is another interesting feature of this compound. That the oxygen adsorbed formed a surface layer was shown by the behaviour of either of the above samples during compression. Each pressure increment caused a large momentary decrease in resistance as shown in Figure 3 where current is plotted against pressure in the first section. The current peaks were probably considerably higher than those shown, as a moderately damped meter was used. The lower points represent the value of the current 30 sec after the pressure increment was applied. Finally, at a constant pressure of 120,000 lb/in², the current decreased with time as shown on the second section of the graph. Apparently each pressure increase resulted in the shearing of the particles of ZrS_2, the oxide layer thereby being disturbed, resulting in lowered resistance. The subsequent increase in resistance and the shape of the curve on the right-hand side of Figure 3 suggest a rapid reoxidation of the ZrS_2. If the sulphide, after surface oxidation had taken place, was pumped to a high vacuum and subsequently opened and the compression test carried out in an argon atmosphere, the current increased on compression as before but showed considerably less decrease with time. If when being pumped the material was heated to about 300 °C prior to opening the testing in argon, the peaks were not observed at all, and the sulphide was found to have a Sp.K. value corresponding to the highest values obtained after the surface oxidation had taken place. Zirconium sesquisulphide and some hafnium compositions behaved similarly, but none of the titanium sulphides did.

(b) Type of Conductivity

Measurements were made to determine whether, in the range 20 to 80 °C, the compounds exhibited metallic or semiconduction. At the conclusion of each Sp.K. test, the plungers compressing the material were heated to 80 °C and the resulting change, if any, in resistance was noted. Four or five heating

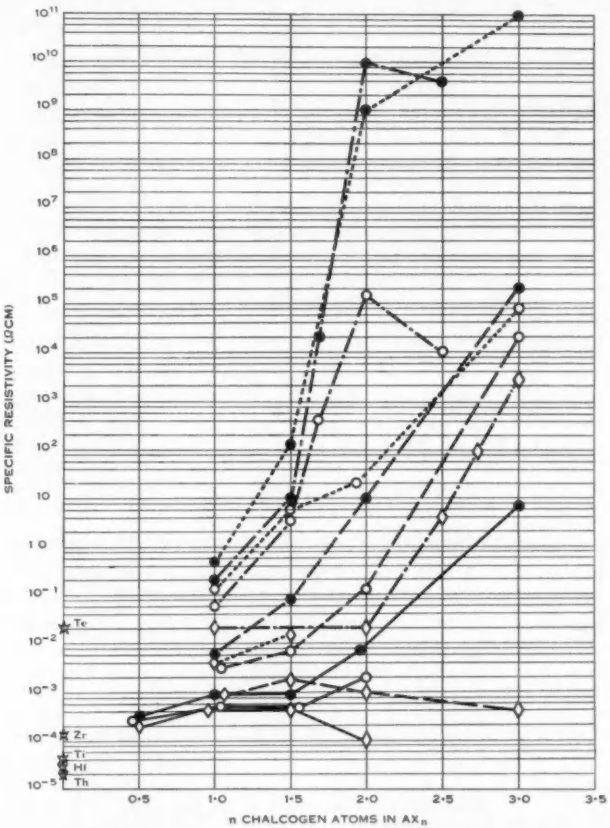

Fig. 1.—Specific resistivities of the chalcogenide compounds.
—— Titanium; – – zirconium; - - - hafnium; –·– thorium;
● sulphide; ○ selenide; ◊ telluride; ✲ specific resistivities of the pure metals.

cycles were carried out. For the reason discussed above, some of the samples had to be measured in argon. The method did not yield very precise results and it was possible to distinguish only between compounds whose conductivity increased noticeably (5 per cent. or greater) and those whose conductivity remained substantially the same or showed a slight decrease. The results are

included in Table 1. Where semiconduction was evident the type, N or P, is noted, this having been determined as described below. Most of the tri- and disulphides and triselenides exhibited conductivity increases of 2 to 4 times in the temperature range used.

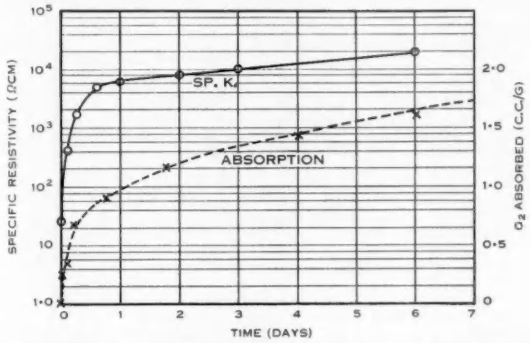

Fig. 2.—Effect of oxygen adsorption on the resistivity of ZrS_3.

(c) *Thermo-e.m.f.'s*

For the measurement of thermo-e.m.f. the samples were pressed into small disks $\frac{1}{4}$ in. diameter and about $\frac{1}{16}$ to $\frac{1}{8}$ in. thick, using pressures of 100,000 lb/in^2. The disks were clamped between platinum contacts, one of which could be heated electrically and the other cooled, if necessary, by a flow of water. Temper-

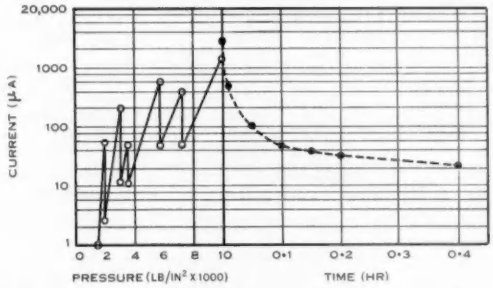

Fig. 3.—Effect of pressure increments on the conductivity of partially oxidized ZrS_3 (left-hand side) and of time (right-hand side).

atures were measured by thermometers inserted into each contact. The e.m.f. was measured by means of a vacuum-tube voltmeter, using a Mullard ME 1400 electrometer tube followed by a D.C. amplifier. The input resistance to the electrometer tube was approximately $10^8\ \Omega$.

It was not possible to determine unequivocally the thermo-e.m.f.'s of the four compounds having the highest resistivities, namely, HfS_3, HfS_2, $ThS_{2\cdot5}$,

and ThS_2. This was in part due to the fact that a change of resistance occurred when the disks were heated and this change of input resistance affected the electrometer tube. It is likely that these four compounds are N-type semiconductors.

The thermo-e.m.f. values are included in Table 1; positive values indicate electrons flowing from platinum to chalcogenide at the hot junction, that is, N-type semiconduction.

(*d*) *Rectification*

Many of the compounds have such high resistivities that front-to-back ratios cannot be measured satisfactorily. Others undergo such rapid surface oxidation that when probes are placed on their surfaces they appear practically insulating. Tests were made for point contact rectification on certain of the materials, using both platinum and tungsten wires etched to fine points.

None of the lower chalcogenides, which were prepared as fine powders and therefore had to be pressed into disks prior to testing, showed any rectifying properties. The remainder can be divided into three classes:

(i) Those grown as single crystals, namely, TiS_3, $ZrTe_3$, and $TiTe_3$. Of these, only TiS_3 showed front-to-back ratios of about 2 : 1 at certain places.

(ii) Materials prepared as crystalline adherent masses. The only ones that exhibited rectification were $TiSe_2$, 1·2 : 1·0, and $ZrSe_3$, 2 : 1.

(iii) Finely crystalline materials produced by degradation of higher chalcogenides—these were compacted prior to testing. Only TiS_2 and $ZrSe_2$ gave front-to-back ratios of about 1·5 : 1.

In all cases the highest resistance resulted when the " whisker " was negative with respect to the chalcogenide. The results indicate no pronounced rectifying properties in this group of materials. The best examples are somewhat analogous to molybdenite in this respect without reaching the efficiency of this compound.

IV. Discussion

(*a*) *Specific Resistivities*

The graphical representation (Fig. 1) of the Sp.K. values demonstrates the following interesting trends:

(i) The increasingly metallic nature of the compounds as one passes from sulphides through selenides to tellurides; the last named, except for $ThTe_{2\cdot5}$, are closely akin to alloys.

(ii) In general, for each Group IV element there is an increasingly metallic tendency as one passes from a higher to a lower chalcogenide.

(iii) The decreasingly metallic, or increasingly saltlike, nature of the compounds from Ti to Zr and Hf and finally Th is evident. It has become customary to define metallic conductivity as being shown by substances having a Sp.K. $<0\cdot01\ \Omega$cm; semiconduction by substances having Sp.K. values from 0·01 to $10^9\ \Omega$cm and insulating properties if the value is above $10^9\ \Omega$cm. If this somewhat arbitrary definition is accepted, then, taking the disulphides as an

example, we have a sequence from metallic for TiS_2, through semiconduction in ZrS_2, to an Sp.K. value for HfS_2 at the extreme end of the semiconduction range, and finally a value of 10^{10} Ωcm for ThS_2, which could therefore be classed as an insulator.

For the tri- and di-compounds, it is possible to construct a useful graphical chart which expresses this sequence of increasingly saltlike characteristics of the compounds, as one passed from titanium to thorium. Such an arrangement is shown in Table 2, in which the compounds $ThS_{2\cdot5}$, $ThSe_{2\cdot5}$, and $ThTe_{2\cdot5}$ are included with the tri-compounds of the other metals. Here, the criterion for an insulator (Sp.K. $>10^9$ Ωcm) has been used for classifying the compounds as " saltlike ".

TABLE 2

TYPE OF CONDUCTION FOR THE TRI- AND DICHALCOGENIDES

Element	Sulphide		Selenide		Telluride	
	Tri or Poly	Di	Tri or Poly	Di	Tri or Poly	Di
Titanium ..	Semi	Metallic	—	Metallic	—	Metallic
Zirconium ..	Semi	Semi	Semi	Semi	Metallic	Metallic
Hafnium ..	Salt	Salt	Semi	Semi	—	—
Thorium.. ..	Salt	Salt	Semi	Semi	Semi	Semi

Some comparisons of interest are not possible, owing to the failure of titanium and hafnium to form certain tri-compounds.

The flattening of some of the curves between the compositions $AX_{1\cdot0}$ and $AX_{1\cdot5}$, especially noticeable for the Ti-Se, Ti-Te, Zr-Se, and Zr-Te systems, may be related to the manner in which the lower chalcogenides in these systems undergo transition. In these compounds there is an interpolation of additional metal atoms into vacant octahedral positions which exist between neighbouring planes of chalcogen atoms as one proceeds towards mono-compounds. Thus entirely different structures are not involved.

It will be seen that in the Th-S and Th-Se systems, the maximum value of Sp.K. occurs for the dichalcogenide. Thorium is the most basic of the four metals and forms compounds which are more stable and saltlike than the corresponding compounds of titanium etc., as may be shown by such examples as (1) the occurrence of stable thorium salts of the oxy acids sulphuric, nitric, etc., (2) the progressively increasing melting points of the tetrahalides ($TiCl_4$, −23 °C; $ZrCl_4$, sub 331 °C; $ThCl_4$, 765 °C), and (3) the fact that ThS_2 does not undergo degradation on heating up to m.p. 1900 °C. Hence it may be expected that the disulphide of thorium, and to a lesser extent the diselenide, are compounds of increased stability in which thorium is exerting its normal valence of four.

On the other hand, any compound containing more sulphur (or selenium) than the di-compound might be expected to have a higher resistivity as is observed for HfS_2, HfS_3, etc.

Although the difference between the measured values of resistivity for TiS_3 single crystals and TiS_3 in the form of compressed powder may be due to lack of intimate contact because of air pockets etc. between particles of the powder, it is possible that the Sp.K. for the single crystals is different along different axes. This possibility is being investigated.

The Th-S and Hf-S systems appear anomalous in that the resistivity values for the lower sulphides of thorium lie below those for the corresponding compounds of hafnium. The same is true of the lower selenides of these metals. However, the magnitudes of the differences are of doubtful significance (except, perhaps, the case of $ThS_{1\cdot5}$ and $HfS_{1\cdot5}$) and the effect is not shown elsewhere.

The system Th-Te merits some comment as it yields the only sample of a " poly " telluride with an *increasing* resistivity. No satisfactory explanation can yet be suggested for this. If a small percentage of metallic tellurium is added to $ThTe_{2\cdot5}$ and the two are mixed by thorough grinding, the resistivity of the product is found to be lower than that of $ThTe_{2\cdot5}$, as would be expected because the Sp.K. of Te is approximately 0·02 Ωcm. However, for compositions containing tellurium in excess of that represented by $ThTe_{2\cdot5}$, which by X-ray analysis show the presence of free tellurium, the resistivity rises progressively with tellurium content until Te : Th = 3 : 1, at which the value is 2000 Ωcm. This phenomenon appears to be associated with the fact that it is difficult to remove the excess tellurium from such materials—heating for more than a week at 600 °C was required to establish a composition $ThTe_{2\cdot5}$. Similar behaviour was found for thorium selenide compositions containing Se : Th $>2\cdot5$ but in these, excess selenium would be expected to cause a rise in resistivity. All other chalcogenides could be separated from excess chalcogen readily as previously reported. Strotzer and Zumbusch (1941) reported the formation of what appeared to be loose compounds of thorium polysulphide and sulphur such as ThS_{10} (violet-brown) and Strotzer, Biltz, and Meisel (1939) thought that $ZrS_{3\cdot5}$ etc. were not merely mechanical mixtures. However, the excess sulphur was readily removed from these " compounds " either by leaching with CS_2 or by a sublimation during which the sulphur pressure was close to the theoretical for the temperature used. Whatever doubts may be cast on the evidence for the existence of such " compounds ", the phenomenon of increasing resistivity with increasing tellurium content may perhaps be regarded as evidence of a new kind to support such contentions.

Eastman *et al.* (1950), who gave no details of their method for determining specific resistivity, claimed that the values for the lower thorium sulphides are all below 10^{-3} Ωcm, namely, Th_7S_{12} and Th_2S_3, 10^{-3} to 10^{-4} Ωcm, ThS $<10^{-4}$ Ωcm. These values appear very low, that for ThS approaching the value for pure thorium metal. As these workers failed to melt ThS it must be assumed that the resistivity measurement was made on a powdered sample. In the other cases their figures may refer to melted materials, which would be expected to yield

lower values than powders, but scarcely of the order of 10^5 to 10^7 lower. Unfortunately, the materials referred to contained considerable amounts of impurities, the effects of which it is difficult to assess.

(*b*) *Type of Conductivity*

Except for the tri- and disulphides of titanium the compounds of this element are all metallic. Zirconium exhibits metallic conductivity in the monoselenide and monosulphide, and all telluride compounds. Hafnium closely resembles zirconium. For thorium the mono-compounds are metallic but the highest telluride is semiconducting. For hafnium and thorium the two highest sulphides, although semiconducting, have resistivities high enough for them to be regarded almost as insulators. In general, therefore, the increase in saltlike properties from titanium to thorium is again evident, as is the increase in metallic nature from sulphur to tellurium.

(*c*) *Thermo-e.m.f.*

The higher sulphides of titanium and zirconium and the two higher selenides of zirconium are N-type semiconductors with large thermo-e.m.f.'s. With hafnium, however, a fundamental change takes place and the triselenide is a P-type semiconductor with a thermo-e.m.f. of magnitude similar to those of the sulphides. From $HfSe_3$ to $HfSe_2$ there is a change from P type to N type, but in the Th-Se system the P type extends also to $ThSe_2$ and the transition to N type occurs at $ThSe_{1.7}$. P-type semiconduction appears, therefore, only with the higher selenides of the more basic metals. It is possible that there are traces of free selenium in $HfSe_3$ and $ThSe_{2.5}$ but this is unlikely in $ThSe_{2.0}$. The analytical data are not sufficiently accurate to determine if these selenides contain a stoicheiometric excess of selenium, and further crystallographic structure data are being accumulated.

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THE SULPHIDES, SELENIDES, AND TELLURIDES OF TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM

IV. LUBRICATION PROPERTIES OF THE GRAPHITIC CHALCOGENIDES

By F. K. McTaggart* and A. Moore†

[*Manuscript received July* 10, 1958]

Summary

The majority of the chalcogenides of Ti, Zr, Hf, and Th having layer lattice structures and/or graphitic nature were tested for possible lubricating properties. Although none of these materials adheres to the common metals, it was shown that the shearing forces necessary to cause sliding between layers are in general low and comparable to those involved in molybdenum disulphide and graphite.

I. Introduction

The good lubricating properties of graphite and molybdenum disulphide, which are layer lattice-type materials, have been known for some time. Peterson and Johnson (1954) measured the frictional properties of a number of other substances and found that the layer lattice compounds $CdCl_2$, CdI_2, $CoCl_2$, $CuBr_2$, PbI_2, and WS_2 give low coefficients of friction when placed between sliding steel surfaces. These compounds also appear to form films on the metal surfaces. However, none was as effective as MoS_2, although WS_2 seemed to merit further investigation as a lubricant. The present paper describes the frictional properties of some of the graphitic compounds found among the chalcogenides of titanium, zirconium, hafnium, and thorium.

II. Materials

The preparation and structures of the titanium, zirconium, and hafnium chalcogenides used in this work have been described by McTaggart and Wadsley (1958). The thorium compounds have recently been prepared and examined (McTaggart, unpublished data). Of the chalcogenides prepared by these authors, those presented in Table 1, when rubbed between the fingers, produced a smooth lustrous texture similar to that produced by graphite and MoS_2. Those marked with an asterisk were chosen for investigation. For comparison a high-grade commercial molybdenum disulphide of fine particle size and a commercial graphite were used.

Comparison of the electronmicrographs (Plates 1 and 2) of the compounds chosen for investigation shows clearly how the trichalcogenides rub out to thin

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ribbonlike particles. This ribbonlike structure appears to persist in one or two of the di-compounds, for example, $ZrSe_2$, probably due to the fact that the latter were all made by thermal degradation from the corresponding tri-compounds. The graphitic structure typical of the dichalcogenides is shown in TiS_2, $TiSe_2$, $TiTe_2$, and $ZrTe_2$.

TABLE 1

GRAPHITIC CHALCOGENIDES

Chalcogenide	Titanium	Zirconium	Hafnium	Thorium
Sulphides	TiS_3*	ZrS_3*	HfS_2	
	TiS_2*	ZrS_2	HfS_2	
Selenides	$TiSe_2$*	$ZrSe_3$*	$HfSe_3$	
		$ZrSe_2$*	$HfSe_2$	
Tellurides	$TiTe_2$*	$ZrTe_3$*		$ThTe_{2\cdot5}$
		$ZrTe_2$		

III. Experimental Procedure and Results

The friction apparatus which was similar to that described by Bowden and Leben (1939) consisted of a $\frac{1}{4}$ in. diameter steel hemisphere DPH 258 sliding over a flat steel surface DPH 145 under a load of 4 kg and at a speed of about 0·1 mm/sec. The steel surfaces were cleaned by abrading on wet carborundum paper, washing in hot water, and allowing the water film to evaporate.

Initial tests were made with up to 10 per cent. solid lubricant (MoS_2, TiS_3, TiS_2, etc.) suspended in pure paraffin oil. Under such conditions it was almost impossible in one passage of the slider to establish a layer of the solid lubricant on the metal and the frictional behaviour resembled closely that of pure paraffin by itself. Attention was then turned to establishing tracks of solid materials by dry rubbing; molybdenum disulphide adhered readily and formed a smooth track after 30 to 40 passes of the plate beneath the hemispherical slider, usually carried out under increasing loads up to a maximum of 4 kg. The coefficient of friction was then about 0·04. When the sulphides, selenides, and tellurides of titanium and zirconium were used in the same way it was found impossible to establish a track. These materials would not adhere to the metal plate and were simply pushed out of the way of the slider. The coefficient of friction was about 0·5.

In order to ensure that sliding between the solid lubricant and the steel should take place, the steel slider was replaced by a compact of the lubricant pressed at 80,000 lb/in^2. Before sliding, it was lightly ground on fine emery paper. The coefficient of friction for graphite was 0·16, for MoS_2 0·2, and for the other materials between 0·30 and 0·54 (see Table 2). Finally, the sliding of the solid lubricant on itself was investigated by using a flat compact of the lubricant as the lower surface. The compact surfaces were rubbed lightly with fine emery paper before use. Under these conditions MoS_2 showed approximately

the same coefficient of friction as many of the other chalcogenides, namely, *c.* 0·20 to 0·25; graphite gave a lower value, namely, 0·08 to 0·09; and the telluride values were higher (Table 2).

The value for MoS_2 confirms a previous measurement of $\mu=0{\cdot}20$ to 0·22 by Feng (1952) for the sliding of a thick layer of this material.

The chalcogenides under investigation were found not to adhere well to copper, brass, stainless steel, silver, titanium, or zirconium.

TABLE 2

COEFFICIENTS OF FRICTION

Lubricant Material	Coefficient of Friction (μ)		Lubricant Material	Coefficient of Friction (μ)	
	Compact of Lubricant on Steel	Compact of Lubricant on Compact of Lubricant		Compact of Lubricant on Steel	Compact of Lubricant on Compact of Lubricant
MoS_2	0·2	0·22	ZrS_2	0·42	0·25
Graphite ..	0·16	0·08–0·09	$ZrSe_2$	0·46	0·25
TiS_3	0·34	0·24	$ZrSe_2$	0·35	0·22
TiS_2	0·31	0·26	$ZrTe_2$	0·54	0·45
$TiSe_2$	0·30	0·21			
$TiTe_2$	0·40	0·37			

IV. DISCUSSION

It is now well established (see, for example, Bowden and Tabor 1950) that the frictional force is dependent on the area of real contact between the sliding surfaces and the shear strength of the junctions found at those points of contact. It has been shown that the combination of low shear strength and small area of real contact, which is obtained with a thin, low-strength film on a hard substrate, will give very low values of the coefficient of friction. This principle, which is applied in the use of thin soft metal films in bearing metals and other bearing surfaces, is also of interest in the use of solid lubricants. Thus MoS_2 will give a low value of friction when present as a thin film between steel surfaces because (i) it adheres to the metal strongly, replacing metal-metal junctions by sulphide-sulphide junctions of approximately equal area, and (ii) in the direction perpendicular to the planes of the crystal layers the bonding is weak and hence low shearing forces will cause movement. However, when sliding as a solid substance on itself the deformation of the relatively soft MoS_2 compacts results in a large area of contact and hence an increase in the coefficient of friction.

The fact that the other chalcogenides tested, except the tellurides, yield coefficients of friction of much the same magnitude as MoS_2, when sliding on themselves, would indicate that bond strengths of similar magnitude exist between their crystal planes. Hence they may be regarded as potential lubricants. They fail, however, to satisfy the second condition for practical

lubrication, namely, the ability to adhere to metal surfaces and so provide junctions other than metal-metal ones.

It is not clear why MoS_2 bonds to metals so readily while such similar compounds as TiS_2 etc. do not. The phenomenon may be related to the adsorption of water vapour. Thus Savage (1948) has shown that graphite loses its lubricating properties in a very dry atmosphere; on the other hand, Peterson and Johnson (1953) demonstrated that MoS_2 is not always effective in humid conditions. It is possible that some of the materials reviewed here may become effective lubricants over certain ranges of water vapour concentration, or by chemical or other modification. If that occurred, some of them offer advantages over MoS_2 for ease of production and grinding.

V. Acknowledgments

The authors wish to acknowledge the help of Miss Joy Bear in the measurement of coefficients of friction, and to thank Mr. J. L. Farrant of the Chemical Physics Section for taking the electronmicrographs.

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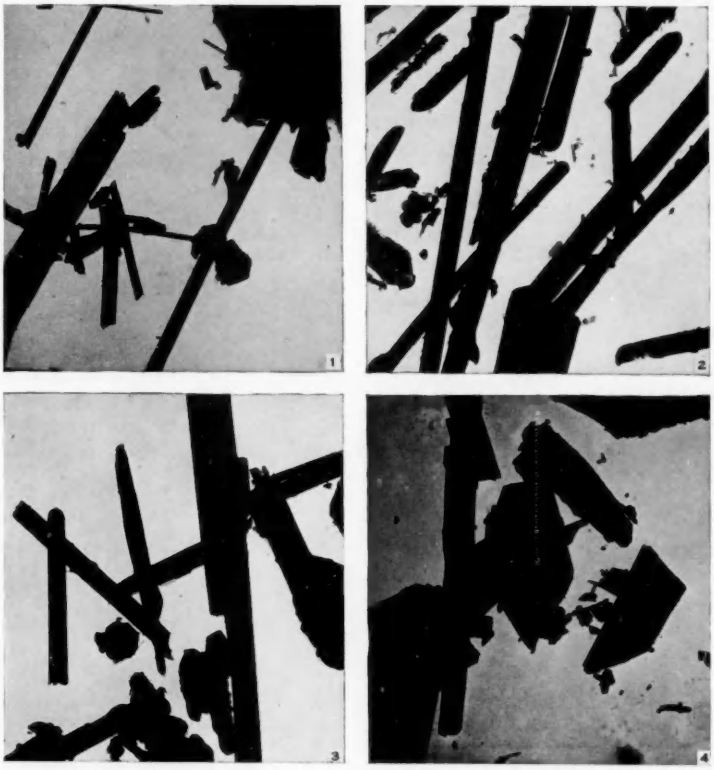
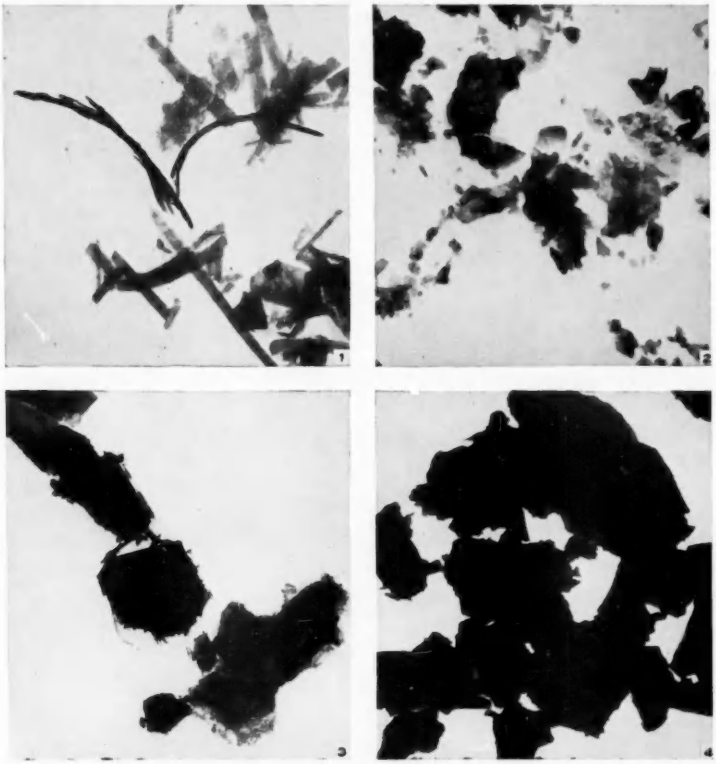
TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM CHALCOGENIDES. IV



Electronmicrographs (×10,000) of graphitic chalcogenides: 1, ZrS_2; 2, $ZrSe_2$; 3, $ZrSe_2$; 4, $ZrTe_2$.

TITANIUM, ZIRCONIUM, HAFNIUM, AND THORIUM CHALCOGENIDES. IV



Electronmicrographs (×10,000) of graphitic chalcogenides: 1, TiS_2; 2, TiS_2; 3, $TiSe_2$; 4, $TiTe_2$.

OXIDATIONS WITH IODOSOBENZENE DIACETATE*

IX. A KINETIC INVESTIGATION OF THE REACTION WITH SUBSTITUTED-2-NITROANILINES

By K. H. PAUSACKER† and J. G. SCROGGIE†‡

[*Manuscript received May* 29, 1958]

Summary

Benzofurazan oxides are formed in excellent yield when certain substituted-2-nitroanilines react with iodosobenzene diacetate in benzene containing 1 per cent. (by volume) of acetic acid. The kinetics of this reaction have been studied. It is considered that the mechanism of the reaction involves a reversible reaction of the 2-nitroaniline with iodosobenzene diacetate to form acetic acid and an intermediate which is then converted to benzofurazan oxide, iodobenzene, and acetic acid. This reaction is therefore similar to the reaction of iodosobenzene diacetate with glycols.

The rates of oxidation of substituted-2-nitroanilines could not be correlated with the electrical effect of the substituent. The reasons for this are discussed in detail.

I. INTRODUCTION

It has previously been found (Pausacker and Scroggie 1954) that a number of 4- and 5-substituted-2-nitroanilines can be oxidized by iodosobenzene diacetate to the corresponding benzofurazan oxides, in almost quantitative yield, when benzene is the solvent. When acetic acid is the solvent, furazan oxides were not formed and only the corresponding azo compounds were isolated in moderate yield (Barlin, Pausacker, and Riggs 1954).

In order to investigate the mechanism of the formation of benzofurazan oxides, it was decided to determine the kinetics of the reaction. The rates of reaction of 2-nitroaniline, 4-chloro-, 5-chloro-, 4-methyl-, 5-methyl-, 4-nitro-, 5-nitro-, and 5-methoxy-2-nitroaniline are reported in the present paper.

II. EXPERIMENTAL

(*a*) *Reagents*

Iodosobenzene diacetate was crystallized from benzene and stored over sodium hydroxide. The minimum purity, estimated iodometrically, was 99 per cent. The following amines were freshly crystallized from an appropriate solvent and the melting point determined. Melting points in parentheses are those reported in the literature: 2-nitroaniline, 72 °C (72 °C); 4-chloro-2-nitroaniline, 116 °C (116 °C); 5-chloro-2-nitroaniline, 126 °C (126 °C); 4-methyl-2-nitroaniline, 117 °C (117 °C); 5-methyl-2-nitroaniline, 110 °C (110 °C);

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‡ This paper represents part of a dissertation submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Melbourne.

5-methoxy-2-nitroaniline, 131 °C (131 °C); 2,4-dinitroaniline, 182 °C (188 °C); 2,5-dinitroaniline, 136 °C (137 °C). Benzene was purified by Vogel's (1950) method. Acetic acid was purified by treatment with chromic acid, followed by boron triacetate (Eichelberger and La Mer 1933), and had m.p. 16·5 °C, corresponding to 0·1 per cent. water content (Rudorff 1870).

(*b*) *Yields of Products*

The appropriate amine ($2{\cdot}8\times10^{-3}$ mol) was added to a solution of iodosobenzene diacetate ($3{\cdot}4\times10^{-3}$ mol) in benzene (200 ml) containing acetic acid (2 mol) and the mixture was kept at 40 °C for 1 day. Benzene was evaporated on the water-bath, and acetic acid and iodobenzene were removed under reduced pressure. The residue was extracted with boiling light petroleum (b.p. 55–70 °C), from which the respective furazan oxides were obtained on cooling. Yields etc. of the benzofurazan oxides are presented in Table 1.

TABLE 1

BENZOFURAZAN OXIDES FORMED BY THE OXIDATION OF SUBSTITUTED-2-NITROANILINES

Substituent:	—	4-Cl	5-Cl	4-Me	5-Me	5-OMe	5-NO_2
M.p. (°C)	70	47	47	96	96	116	70
M.p. (lit. °C)	72	48	48	97	97	118	72
Yield (%)	90	92	91	94	94	92	90

2,4-Dinitroaniline is only sparingly soluble in benzene and was oxidized in solutions more dilute than those used above. Thus, 2,4-dinitroaniline ($3{\cdot}2\times10^{-3}$ mol) was reacted with iodosobenzene diacetate ($3{\cdot}6\times10^{-3}$ mol) in benzene (1 l.) containing acetic acid (1·6 ml) and the nitrobenzofurazan oxide (m.p. 69 °C) was formed in 89 per cent. yield.

(*c*) *Apparatus*

A bath was used whose temperature was controlled to within $\pm0{\cdot}05$ °C. The reactions were performed in calibrated standard 100-ml or 250-ml flasks.

(*d*) *Methods of Estimation*

(i) *General Method.*—The amine ($2{\cdot}00\times10^{-3}$ mol) was weighed into the reaction flask (100 ml) and dissolved in benzene (*c.* 45 ml). When the flask and contents had reached the temperature of the bath, a preheated solution of iodosobenzene diacetate (*c.* $2{\cdot}3\times10^{-3}$ mol) in benzene (50 ml) containing acetic acid (1 ml) was added. Preheated benzene was added to make up to the mark. Aliquot portions (10 ml) were withdrawn at definite times and added to acidified potassium iodide solution. The iodine liberated was titrated with 0·0446N sodium thiosulphate (starch). The original stock solution of iodosobenzene diacetate was also estimated in this way, and was quite stable at the various temperatures used. The reaction of benzofurazan oxide with acidified potassium iodide (Hammick, Edwardes, and Steiner 1931) was negligible under the conditions used for the estimation.

(ii) *Method for 2,4-Dinitroaniline.*—As 2,4-dinitroaniline could not be treated as above, due to the low solubility in benzene, the use of more dilute solutions became necessary. Either the same solvent system may be used, that is, benzene containing 1 per cent. (by volume) of acetic acid or, alternatively, a solvent containing the same molar ratio of acetic acid to amine (and iodosobenzene diacetate) as was used above. The latter system was chosen and 2,4-dinitroaniline ($8{\cdot}00\times10^{-4}$ mol) was dissolved in benzene (*c.* 195 ml) and a solution of iodosobenzene diacetate ($9{\cdot}10\times10^{-4}$ mol) in benzene (50 ml) containing acetic acid (0·4 ml) was added. The flask (250 ml) was made up to the mark with benzene and aliquot portions (25 ml) were withdrawn at definite times and added to acidified potassium iodide. The iodine liberated was titrated with 0·01797N sodium thiosulphate (starch).

TABLE 2

RATES OF OXIDATION OF SUBSTITUTED-2-NITROANILINES BY IODOSOBENZENE DIACETATE

Substituent	$10^5k'$ (sec^{-1})			Log *A*	*E* (kcal)
	25·05 °C	34·95 °C	45·05 °C		
—	9·58	35·1	126	13·77	24·29
	9·60	35·2	126		
4-Chloro- ..	9·71	36·9	133	14·01	24·59
	9·74	37·3	131		
5-Chloro- ..	7·82	31·0	114	14·39	25·24
	7·79	31·2	113		
4-Methyl- ..	12·8	46·9	154	13·21	23·32
	13·0	46·7	152		
5-Methyl- ..	7·28	28·5	101	13·89	24·59
	7·51	28·6	99·6		
5-Methoxy-..	6·57	24·5	89·0	13·81	24·56
	6·55	24·5	88·6		
4-Nitro- ..	10·6	30·2	69·2	8·93	17·60
	10·7	30·3	71·1		
5-Nitro- ..	6·73	28·6	107	14·84	25·93
	6·88	28·7	106		

(*e*) *Results*

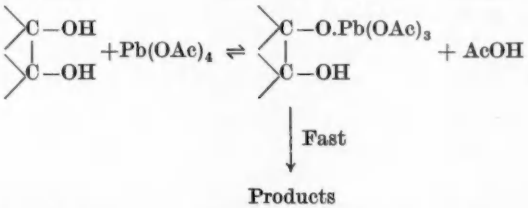
Reactions at 25 °C were followed in the range of *c.* 10–30 per cent. completion and at higher temperatures in the range of *c.* 10–60 per cent. completion. With the exception of 2,4-dinitroaniline, the reaction was not second order but all the results were found to obey the derived equation (**5**) (see Section III). At least five, and usually more than five, rate constants were calculated at different

times and then averaged in order to obtain the rate constant k' quoted in Table 2. The deviation from the average was 2–5 per cent. and duplicate results are recorded. The k' values obey the Arrhenius equation and the various A and E values are shown in Table 2.

III. Discussion

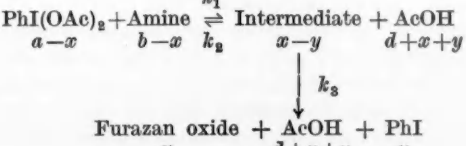
(a) *Kinetics of the Reaction*

One of us (Scroggie 1954) has already investigated the rate of oxidation of certain 2-nitroanilines in benzene without the addition of any acetic acid. Second-order kinetics were not obeyed as the calculated second-order rate constants decreased as the reaction proceeded. This suggested that the first stage of the reaction may be a reversible reaction involving acetic acid (cf. Pausacker and Scroggie 1954). As acetic acid accumulates in the reaction mixture, it will therefore cause the calculated second-order rate constants to continually decrease. This finding compares with the results quoted by Criegee (1934) who found that, when glycols are oxidized by lead tetra-acetate in benzene and other inert solvents, second-order kinetics were not observed and these could only be obtained when a kinetic excess of acetic acid was present. Furthermore, Criegee postulated that the reversible formation of an intermediate "ester" occurs in this reaction:



In the present work, it was thought desirable to use a kinetic excess of acetic acid but care must be taken that too much acetic acid is not added for it has been found (Barlin, Pausacker, and Riggs 1954) that azo compounds, rather than benzofurazan oxides, are formed when some 2-nitroanilines are oxidized in acetic acid solution. In addition, the rate of oxidation decreases markedly with increasing concentration of acetic acid and, in order to avoid using excessively high temperatures, benzene containing 1 per cent. (by volume) of acetic acid was chosen as solvent. Excellent yields of benzofurazan oxides were obtained (see Table 1) but second-order kinetics were not obeyed as the molar concentration of acetic acid is only 8·7 times that of the 2-nitroaniline.

In order to test the proposed mechanism the following kinetic equation was derived:



a, b, and d are the initial concentrations (mol l^{-1}) of iodosobenzene diacetate, amine, and acetic acid respectively; and x and y are the amounts of iodosobenzene diacetate used and furazan oxide formed at time t (sec).

The following expression may then be derived:

$$d(x-y)/dt=k_1(a-x)(b-x)-k_2(x-y)(d+x+y)-k_3(x-y), \quad .. \quad (1)$$

and

$$dy/dt=k_3(x-y). \quad ..... \quad (2)$$

It is assumed that a steady state involving the intermediate is reached, that is,

$$d(x-y)/dt=0,$$

and

$$x-y\simeq 0.$$

Under these conditions, (1) and (2) may be combined as follows:

$$\frac{dx}{dt}=\frac{k_1k_3(a-x)(b-x)}{k_3+k_2(d+2x)}. \quad ..... \quad (3)$$

On integration this gives

$$t=\frac{2\cdot303}{k_1k_3(a-b)}\left[(k_3+k_2d+2bk_2)\log\frac{b}{b-x}-(k_3+k_2d+2ak_2)\log\frac{a}{a-x}\right]. \quad ..... \quad (4)$$

If it is assumed that $k_2 \gg k_3$, equation (4) becomes

$$k'=\frac{2\cdot303}{(a-b)t}\left[(d+2b)\log\frac{b}{b-x}-(d+2a)\log\frac{a}{a-x}\right], \quad ..... \quad (5)$$

where $k'=k_1.k_3/k_2$.

This expression, which was used to calculate the rate constants k' reported in Table 2, is essentially the same as that used by Criegee (1934) for the oxidation of glycols by lead tetra-acetate in benzene solution.

The mechanism proposed for this reaction is thus supported by the following facts: (i) second-order kinetics were not obeyed in benzene solution, (ii) the rate is decreased by the addition of acetic acid, and (iii) the kinetics indicated by equation (5) are obeyed. It is intended to discuss the probable structure of the intermediate in a later paper.

The oxidation of 2,4-dinitroaniline in benzene-acetic acid also obeyed second-order kinetics, which means that the first stage of this reaction need not necessarily be regarded as reversible.

(*b*) *Effect of Substituents*

It is seen (Table 2) that there is no simple effect of substituents on the rate of oxidation of the various 2-nitroanilines investigated, for the order of rates is 5-OMe<5-NO_2<5-Me<5-Cl<H<4-Cl<4-NO_2<4-Me at 25 °C and yet is 4-NO_2<5-OMe<5-Me<5-NO_2<5-Cl<H<4-Cl<4-Me at 45 °C. Furthermore, the log A values vary from 8·93–14·84 while there is a corresponding variation

(17·60–25·93 kcal) in E. The relationship between log A and E is, in fact, linear and this has been definitely established by evaluating the correlation coefficient "r" (Leffler 1955) as 1·00. This linear relationship indicates that there is a substituent isokinetic relationship (Leffler 1955) existing among these various reactions. This means that there should be a temperature, known as the "isokinetic temperature" β at which all reactions will proceed at the same rate. This temperature can be simply calculated from the log A and E values (Leffler 1955; Pausacker 1958) and, using the method of least squares, was found to be 34 °C. This temperature is actually within the range at which the rate constants were measured and so the variations in rate with change of substituent are not significant. It is therefore impossible to draw any conclusions as to the effect of substituents on the rate of the reaction, for the temperatures at which measurements were made are all too close to the isokinetic temperature. Random deviations in the rate constants are expected due to slight departures from the strict isokinetic relationship. It should be noted that these remarks may not be strictly applicable to the oxidation of 2,4-dinitroaniline as a different solvent system was used (see Section II (*d*) (ii)).

IV. Acknowledgments

One of us (J.G.S.) thanks Imperial Chemical Industries Australia and New Zealand for the award of a Research Fellowship and the University of Melbourne for a Research Grant.

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OXIDATIONS WITH IODOSOBENZENE DIACETATE*

X. THE OXIDATION OF 3(OR 6)-SUBSTITUTED-2-NITROANILINES

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Summary

The oxidation of eight 3(or 6)-substituted-2-nitroanilines with iodosobenzene diacetate, in both benzene and acetic acid solution, has been investigated. Benzofurazan oxides and azo compounds were produced in varying yields. Certain of these amines have also been oxidized with iodosobenzene diacetate in other solvents, and with sodium hypochlorite in ethanolic potassium hydroxide. Six of these 3(or 6)-substituted-2-nitroanilines have been oxidized with lead tetra-acetate, in both benzene and acetic acid solution, and varying yields of azo compounds were obtained. Benzaldehyde was isolated from the oxidation of benzylamine with iodosobenzene diacetate, in either benzene or acetic acid solution. The mechanisms of these reactions are discussed. New methods of synthesizing 6-methoxy-2-nitroaniline and 3-methoxy-2-nitroaniline are described.

I. INTRODUCTION

It has been found (Pausacker and Scroggie 1954*b*) that many 4- and 5-substituted-2-nitroanilines are converted to the corresponding benzofurazan oxide in excellent yield when oxidized by iodosobenzene diacetate in benzene solution. When acetic acid was the solvent, only moderate yields of the corresponding azo compound could be isolated (Barlin, Pausacker, and Riggs 1954).

The present investigation is an extension of this work and is aimed at investigating the effect of 3- and 6-substituents on the mode of oxidation of 2-nitroanilines. The effect of solvent variation has been examined with a view to substantiating the mechanisms proposed previously and the use of lead tetra-acetate as a convenient reagent for the preparation of symmetrical azo compounds has been studied further.

II. EXPERIMENTAL

All melting points are corrected. Unless otherwise specified, the light petroleum was fraction, b.p. 55–77 °C. Analyses are by the C.S.I.R.O. Microanalytical Laboratory at the University of Melbourne.

(*a*) *Preparation of 3(or 6)-Substituted-2-nitroanilines*

(i) *3-Chloro-2-nitroaniline.*—Acid-catalysed rearrangement of 3-chlorophenylnitramine produced a mixture of chloronitroanilines, from which the steam-involatile 3-chloro-4-nitroaniline (19%) was isolated. The steam distillate was separated, by repeated chromatography in benzene-ethyl acetate on alumina, into 5-chloro-2-nitroaniline (50%) and 3-chloro-2-nitroaniline (10%).

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The latter amine crystallized from benzene-light petroleum as fine yellow needles, m.p. 108·0–108·5 °C (Found: C, 42·1; H, 3·1%. Calc. for $C_6H_5ClN_2O_3$: C, 41·8; H, 2·9%). This method of preparation is essentially that which was kindly communicated to us by Dr. S. H. Harvey.

(ii) *3-Methoxy-2-nitroaniline.*—(1) 3-Methoxy-2-nitrobenzoic acid (1·00 g) was dissolved in concentrated sulphuric acid (8·5 ml) and chloroform (17 ml), and warmed to 50 °C. Sodium azide (0·40 g) was slowly added (20 min) to the stirred solution, which was then poured onto ice and filtered to recover unchanged acid (0·07 g). Basification of the filtrate (NaOH), followed by ether-extraction, recovered 0·35 g dark orange solid, m.p. 92–118 °C. Chromatography of the benzene solution on alumina gave a yellow band, which eluted readily to yield *3-methoxy-2-nitroaniline*, which crystallized from light petroleum as fine yellow needles (0·29 g), m.p. 124·0–124·5 °C (Found: C, 50·1; H, 4·9; N, 16·9%. Calc. for $C_7H_7N_2O_3$: C, 50·0; H, 4·8; N, 16·7%).

(2) 3-Methoxy-2-nitrobenzoic acid (9·1 g), thionyl chloride (4·2 ml), and sodium-dried benzene (300 ml) were refluxed together for 3 hr. Treatment of the cooled solution with ammonia (9·0 ml; d=0·880) precipitated *3-methoxy-2-nitrobenzamide* (7·2 g), which crystallized from water or ethanol, as colourless needles, m.p. 212·5–213·0 °C (Found: C, 49·2; H, 4·2; N, 14·4%. Calc. for $C_8H_8N_2O_4$: C, 49·0; H, 4·1; N, 14·3%). Unchanged acid (1·5 g) was recovered.

The amide (0·500 g) was shaken with aqueous 2N sodium hydroxide (5 ml), *tert.*-butanol (10 ml), and *tert.*-butyl hypochlorite (0·60 ml) at 50 °C for 1 hr; the reaction mixture was then diluted with water (50 ml) and extracted with ether to recover 0·30 g orange-yellow oily solid which was chromatographed in benzene on alumina. A very pale yellow band eluted rapidly to yield *4-methoxybenzofurazan oxide* (0·09 g), crystallizing from light petroleum as pale yellow, flattened needles, m.p. 125·5–126·0 °C (Found: C, 50·6; H, 3·7; N, 17·4%. Calc. for $C_7H_6N_2O_2$: C, 50·7; H, 3·6; N, 16·9%). A second yellow band was eluted to yield 3-methoxy-2-nitroaniline (0·12 g), m.p., and mixed m.p. with an authentic specimen, 124·0–124·5 °C.

When the above amide (0·500 g) was reacted with sodium hydroxide (10 ml; 2·5N) and sodium hypochlorite (10 ml; 0·50N) at 40 °C for 2 hr, only 4-methoxybenzofurazan oxide (0·28 g), m.p. and mixed m.p. 125–126 °C, was isolated.

(iii) *6-Methoxy-2-nitroaniline.*—6-Methoxy-2-nitrobenzonitrile (10·0 g), ethanol (400 ml), and sodium hydroxide (2 g) were heated together on a water-bath at 65–70 °C, and hydrogen peroxide (80 ml; 28%) was added dropwise over a period of 30 min. After standing at 65–70 °C for a further 4 hr, the reaction mixture was carefully neutralized (conc. HCl) to Congo red and concentrated by distillation until no more crystals could be obtained. 6-Methoxy-2-nitrobenzamide (7·2 g) was obtained as colourless crystals (from EtOH), m.p. 202·0–202·5 °C (lit. 195 °C) (Found: C, 49·3; H, 4·0; N, 14·2%. Calc. for $C_8H_8N_2O_4$: C, 49·0; H, 4·1; N, 14·3%).

The amide (6·1 g) was treated with aqueous 2N sodium hydroxide (60 ml), *tert.*-butanol (60 ml), and *tert.*-butyl hypochlorite (7·5 ml). A deep red colour developed immediately, and external cooling was necessary to keep the temperature below 50 °C. After maintaining the temperature at 45–50 °C for a further 2 hr, with frequent shaking, the reaction mixture was cooled and extracted with ether. The extract was purified by chromatography in benzene on alumina, yielding 6-methoxy-2-nitroaniline as fine pale orange needles (aqueous EtOH), m.p. 75·5–76·0 °C (lit. m.p. 75–76 °C) (Found: C, 50·2; H, 4·7%. Calc. for $C_7H_7N_2O_3$: C, 50·0; H, 4·8%). Acetyl derivative, m.p. 157–158 °C (lit. 156 °C).

(iv) *Nitration of 3-Methoxyacetanilide.*—3-Methoxyacetanilide (25·5 g) was nitrated by the method of Reverdin and Widmer (1913) at 10 °C, and 3-methoxy-4-nitroacetanilide (3·5 g; m.p. 124–125 °C) was extracted from the product with hot ligroin. The residue was hydrolysed with 15% hydrochloric acid, and the free amines were extracted with hot benzene (3 l.). 3-Methoxy-2,4-dinitroaniline (4·2 g; m.p. 156–157 °C) crystallized on cooling and the filtrate was chromatographed on alumina. A yellow band, with an orange leading edge, was observed. 3-Methoxy-4-nitroaniline (0·26 g; m.p. 130–131 °C) was obtained by elution of the leading edge, and

3-methoxy-2,4-dinitroaniline (0·85 g; m.p. 156–157 °C) was obtained from the yellow band. An attempt to nitrate 3-methoxyacetanilide at 3 °C was unsuccessful.

The structure of 3-methoxy-2,4-dinitroaniline was confirmed by examination of the infra-red spectrum in a "Nujol" mull. The spectrum was examined with a single-beam, double-pass, Perkin-Elmer spectrometer, using a sodium chloride prism. The strong C—H absorption at 830 cm^{-1}, characteristic of a 1,2,3,4-substituted-benzene, was observed. Other absorption peaks (cm^{-1}) were at 1623, 1605, 1572, 1511, 1495, 1439, 1427, 1284, 1219, 1172, 1129, 1099, 1020, 953 (weak), 839 (weak), 816 (weak), 755, 734 (weak), and 694. The symmetric N—O stretching frequency, expected near 1350 cm^{-1}, could not be measured since the absorption was very weak.

(*b*) *Oxidations of 3(or 6)-Substituted-2-nitroanilines with Iodosobenzene Diacetate in Benzene Solution*

The powdered amine (1·00 g) was dissolved in 100–200 ml dry, thiophen-free benzene in which 1·1 mol of iodosobenzene diacetate per mol of amine had previously been dissolved. The uptake of oxidant was followed by iodometric titration of 1 ml aliquots. If the oxidant titre did not decrease by 30% during the first day at room temperatures, the reaction flask was placed in an incubator and the temperature increased until appreciable uptake of oxidant commenced. When uptake of oxidant was complete, the products were isolated by distilling off the solvent from a water-bath; acetic acid was similarly removed at reduced pressure (water-pump). The residue was extracted with three 60-ml portions of hot benzene; the extract was concentrated to 60 ml, cooled, filtered, and chromatographed on alumina. Benzofurazan oxides and azo compounds appeared in the lowest band, followed by any remaining amine; 2,6-dinitroaniline, however, was only separated from 4-nitrobenzofurazan oxide by repeated chromatography, and formed the lower band. The mixtures of azo compound and benzofurazan oxide which were sometimes obtained were easily separated by sublimation.

The material which did not elute from alumina with benzene was Soxhlet-extracted with ethanol; further extraction of the alumina with acetic acid was sometimes required. Characterizable materials could not be isolated from these extracts by sublimation.

Characterizable products were identified either by mixed m.p. determination or by elemental analysis; the yields of these products are given in Table 1. Unidentified products have been listed together as "high molecular weight material". Acetic acid extracts have been listed separately since they contain some aluminium. Yields have been corrected for the removal of aliquots.

(*c*) *Oxidations of 3(or 6)-Substituted-2-nitroanilines with Iodosobenzene Diacetate in Acetic Acid Solution*

The powdered amine (1·00 g) was dissolved in an acetic acid solution containing 1·1 mol of iodosobenzene diacetate per mol of amine. When oxidation was complete, the products were isolated as indicated in Subsection (*b*). In the instance of 3-methyl-2-nitroaniline, the amine and corresponding azo compound formed a mixed band, but the amine was readily separated by sublimation. The results are presented in Table 2.

(*d*) *Oxidations of 3(or 6)-Substituted-2-nitroanilines with Lead Tetra-acetate in Benzene Solution*

The powdered amine (1·00 g) was dissolved in a solution of lead tetra-acetate (1·1 mol/mol of amine) in sodium-dried, thiophen-free benzene; the oxidation was then carried out as in Section II (*b*). A "blank" solution of lead tetra-acetate in benzene was kept under identical temperature conditions; titration of aliquots showed the oxidant titre to fall slowly. The reaction temperature was increased until the rate of decrease in oxidant titre of the oxidation run appreciably exceeded the rate of decrease in titre of the "blank" solution. When oxidation was complete, the reaction mixture was filtered to remove insoluble material, which was extracted with hot water to remove lead acetate. The filtered benzene solution was treated as in Section II (*b*). The results are summarized in Table 3.

TABLE 1

OXIDATIONS OF 3(OR 6)-SUBSTITUTED-2-NITROANILINES WITH IODOSOBENZENE DIACETATE IN BENZENE SOLUTION

Substituent	Temp. (°C)	Reaction Time (days)	Benzofurazan Oxide (%)	Yield Azo Compound (%)	Recovered Amine (%)	High Mol. Wt. Materials (g)*
3-Cl ..	20	2	49†	35‡	—	0·14
3-OCH_3 ..	20	6	33	11§	—	0·19 (1·0)
3-CH_3 ..	28	6	42‖	28¶	—	0·13
3-NO_2 ..	20	4	93**	—	—	—
6-Cl ..	45	19	86	—	—	—
6-OCH_3 ..	28	3	2	—	18	0·69 (0·50)
6 CH_3 ..	31	7	—	—	53	0·26 (0·80)
6-NO_2 ..	50	8	11	—	79	—

* The values given in parentheses are weights of acetic acid extracts.

† *4-Chlorobenzofurazan oxide* crystallized from methanol as stout yellow needles, m.p. 77·0–77·5 °C (Found: C, 42·2; H, 2·1%. Calc. for $C_6H_3ClN_2O_2$: C, 42·2; H, 1·8%).

‡ *2,2'-Dinitro-3,3'-dichloroazobenzene* crystallized from benzene as orange prisms, m.p. 266·5–267·2 °C (Found: C, 42·6; H, 2·1%. Calc. for $C_{12}H_6Cl_2N_4O_4$: C, 42·2; H, 1·8%).

§ *2,2'-Dinitro-3,3'-dimethoxyazobenzene* crystallized from benzene as flat, orange prisms, m.p. 267–268 °C (Found: C, 50·9; H, 3·7%. Calc. for $C_{14}H_{12}N_4O_6$: C, 50·7; H, 3·6%).

‖ *2,2'-Dinitro-3,3'-dimethylazobenzene* crystallized from acetone as orange plates, m.p. 234·5–235·0 °C (Found: C, 55·7; H, 4·4%. Calc. for $C_{14}H_{12}N_4O_4$: C, 56·0; H, 4·0%).

¶ 4-Methylbenzofurazan oxide crystallized from methanol or light petroleum as pale yellow needles, m.p. 59·5–60·0 °C (lit. 60 °C) (Found: C, 56·0; H, 4·1%. Calc. for $C_7H_6N_2O_2$: C, 56·0; H, 4·0%).

** 4-Nitrobenzofurazan oxide crystallized from ethanol as bright yellow plates, m.p. 145·0–145·5 °C (lit. 143 °C) (Found: C, 40·0; H, 1·9%. Calc. for $C_6H_3N_3O_4$: C, 39·8; H, 1·7%).

TABLE 2

OXIDATIONS OF 3(OR 6)-SUBSTITUTED-2-NITROANILINES WITH IODOSOBENZENE DIACETATE IN ACETIC ACID SOLUTION

Substituent	Temp. (°C)	Reaction Time (days)	Yield Azo Compound (%)	Recovered Amine (%)	High Mol. Wt. Material (g)*
3-Cl	35	5	15	12	0·40 (0·67)
3-OCH_3 ..	20	1	17	—	1·42
3-CH_3 ..	20	1	18	3†	0·63 (0·27)
3-NO_2	45	5	—	9	0·64 (0·20)
6-Cl	35	7	—	49	0·37 (0·06)
6-OCH_3 ..	20	0·1	—	23	0·77 (0·29)
6-CH_3 ..	20	1	—	33	0·73
6-NO_2	118	0·3	—	97	0·11

* The values given in parentheses are weights of acetic acid extracts.

† A 0·9% yield of 3-methyl-2-nitroacetanilide, m.p. and mixed m.p. 126–127 °C, was isolated by sublimation from both the ethanol and acetic acid extracts of brown bands at the top of the chromatogram.

(e) Oxidations of 3(or 6)-Substituted-2-nitroanilines with Lead Tetra-acetate in Acetic Acid Solution

Oxidations were carried out by adding the powdered amine (1·00 g) to a solution of lead tetra-acetate (1·1 mol/mol of amine) in acetic acid (200–250 ml) and proceeding as in Section II (*b*). Aliquots taken from a solution of lead tetra-acetate, alone, in acetic acid revealed no decrease in oxidant titre, even after several weeks at 55 °C.

When oxidation was complete, the solvent was removed by distillation from a water-bath at reduced pressure (water-pump). Since the amines used in the present investigation are slightly volatile in acetic acid, the distillate was, as in Section II(*c*), redistilled. The residues from the two distillations were combined and treated as in Subsection (*d*). The results are tabulated in Table 4.

TABLE 3

OXIDATIONS OF 3(OR 6)-SUBSTITUTED-2-NITROANILINES WITH LEAD TETRA-ACETATE IN BENZENE SOLUTION

Substituent	Temp. (°C)	Reaction Time (days)	Yield Azo Compound (%)	Recovered Amine (%)	High Mol. Wt. Material (g)*
3 CH_3 ..	47	7	41	3	0·52
3-NO_2 ..	80	2	15†	35	0·50
6-Cl	55	16	7‡	49	0·30 (0·18)
6-OCH_3 ..	47	2	—	19	0·54 (0·55)
6-CH_3 ..	39	6	21§	26	0·19 (0·39)
6-NO_2	55	3	—	100	—

* The values given in parentheses are weights of acetic acid extracts.

† *2,2′,3,3′-Tetranitroazobenzene* crystallized from acetone as fine, pale orange needles, m.p. 272·5–273·0 °C (decomp.) (Found: C, 39·7; H, 1·8; N, 23·1%. Calc. for $C_{12}H_6N_8O_8$: C, 39·8; H, 1·7; N, 23·2%).

‡ *2,2′-Dinitro-6,6′-dichloroazobenzene* crystallized from aqueous ethanol as feathery orange needles, m.p. 158·5–159·0 °C (Found: C, 42·1; H, 1·9%. Calc. for $C_{12}H_6Cl_2N_4O_4$: C, 42·2; H, 1·8%).

§ *2,2′-Dinitro-6,6′-dimethylazobenzene* crystallized from ethanol as fine orange needles, m.p. 202·0–202·5 °C (Found: C, 55·9; H, 4·2; N, 18·6%. Calc. for $C_{14}H_{12}N_4O_4$: C, 56·0; H, 4·0; N, 18·7%).

(f) Oxidations with Iodosobenzene Diacetate in Various Solvents

The oxidations were carried out, and the products isolated, as in Section II (*b*). All oxidations were at 20 °C. All solvents were rigorously purified by standard procedures. The results are presented in Table 5.

(g) Oxidations with Sodium Hypochlorite

(i) *Oxidation of 3-Methyl-2-nitroaniline.*—The amine (1·00 g) was dissolved in a saturated ethanolic solution of potassium hydroxide (50 ml). The deep red colour which appeared after 20 sec was discharged by shaking with sodium hypochlorite (24 ml; 1·2M) added portionwise (10 min). The pale cream precipitate was filtered off and washed with cold water to give 4-methylbenzofurazan oxide (0·13 g), m.p. and mixed m.p. 59–60 °C after crystallization from light petroleum. Acidification of the filtrate salted out a further 0·25 g of this product. Benzene-extraction of the filtrate recovered 0·47 g solid, from which the benzofurazan oxide (0·39 g) was isolated by sublimation (80 °C/1·8 mm). The black residue did not contain any azo compound.

(ii) *Oxidation of 6-Methyl-2-nitroaniline.*—When the amine (1·00 g) was dissolved in saturated ethanolic potassium hydroxide (50 ml), a red colour developed after 30 sec. A very intense red

colour developed on addition of sodium hypochlorite (1·2M), and faded to a pale red colour only after addition of 40 ml of the oxidant (40 min). Only inorganic chlorides were precipitated. Benzene extraction recovered a solid (0·27 g), which was chromatographed in benzene on alumina. A yellow band eluted rapidly, and the eluate yielded a solid (0·19 g) which on sublimation (100 °C/2·5 mm), yielded 4-methylbenzofurazan oxide (0·13 g), m.p. and mixed m.p. 59–60 °C. The residue crystallized from ethanol as orange needles of 2,2′-dinitro-6,6′-dimethylazobenzene

TABLE 4

OXIDATIONS OF 3(OR 6)-SUBSTITUTED-2-NITROANILINES WITH LEAD TETRA-ACETATE IN ACETIC ACID SOLUTION

Substituent	Temp. (°C)	Reaction Time (days)	Yield Azo Compound (%)	Recovered Amine (%)	High Mol. Wt. Material (g)*
3-CH_3 ..	20	0·7	16	16	0·35 (0·36)
3-NO_2 ..	55	2	—	—	1·01
6-Cl ..	55	4	—	73	0·13
6-OCH_3 ..	20	0·1	—	18	0·25 (0·33)
6-CH_3 ..	20	3	11	30	0·80
6-NO_2 ..	118	0·2	—	92	0·03

* The values given in parentheses are weights of acetic acid extracts.

TABLE 5

OXIDATIONS OF NITROAMINES WITH IODOSOBENZENE DIACETATE IN SOLVENTS OF VARYING DIELECTRIC CONSTANT ε

Amine	Solvent	ε	Reaction Time (hr)	Yield (%)		High Mol. Wt. Materials (g)
				Furazan Oxide	Azo Compound	
3 - Methyl - 2-nitroaniline	Benzene ..	2·17	140	42	28	0·13
	Chlorobenzene	5·6	12	48	31	0·24
	Acetone ..	17·7	2	72	1	0·17
	Acetonitrile	38·8	48	10	14	0·74
2 - Nitro - 1 - naphthylamine	Benzene* ..	2·17	120	7	3	—
	Acetone ..	17·7	2	6†	—	0·56‡

* Pausacker and Scroggie (1954*b*); the high mol. wt. material was not weighed.

† Naphthofurazan oxide crystallized from light petroleum as pale yellow needles, m.p. and mixed m.p. 125–126 °C.

‡ 35% of the amine was recovered.

(0·05 g), m.p. and mixed m.p. 199–200 °C. The aqueous residue was acidified and benzene-extracted to yield a dark red gum (0·77 g). Chromatography in benzene on alumina produced two pale yellow bands. The lower band yielded a dark red oil (0·37 g) and the upper band a yellow gum (0·02 g). Neither product would yield a crystalline compound, and both contained chlorine.

(iii) *Oxidation of 2,3-Dinitroaniline.*—The amine (1·00 g) was dissolved in saturated ethanolic potassium hydroxide (40 ml), a deep red colour appeared immediately. Addition of sodium

hypochlorite (1·2M) initially intensified the colour but, after addition of 100 ml of the oxidant (20 min), the colour was discharged. Benzene-extraction gave a red gummy solid (0·43 g). Chromatography in benzene on alumina produced a yellow band, from which a yellow solid (0·30 g), m.p. 92–95 °C, was obtained. The product crystallized from aqueous methanol (charcoal) as a crystalline powder, m.p. 101–102 °C. The analysis corresponds to *X-chloro-4-ethoxybenzofurazan oxide* (Found : C, 44·8 ; H, 3·3 ; Cl, 16·5%. Calc. for $C_8H_7ClN_2O_3$: C, 44·8 ; H, 3·3 ; Cl, 16·6%).

Acidification of the aqueous residue, followed by benzene-extraction, recovered an intractable red gum (0·26 g) containing chlorine.

(iv) *Oxidation of 2,6-Dinitroaniline.*—The intense red colour of the solution in saturated ethanolic potassium hydroxide was not discharged by addition of sodium hypochlorite. No pure products were isolated by the procedure outlined in Section II (*g*) (iii), and all fractions contained chlorine.

TABLE 6

ULTRAVIOLET SPECTRA OF SUBSTITUTED-2-NITROANILINES IN CYCLOHEXANE SOLUTION

Substituent in 2-Nitroaniline	Maxima		Minima		Substituent in 2-Nitroaniline	Maxima		Minima	
	Wavelength (mμ)	Log_{10} ε	Wavelength (mμ)	Log_{10} ε		Wavelength (mμ)	Log_{10} ε	Wavelength (mμ)	Log_{10} ε
——	230	4·23	260	3·60	6-Chloro-	231·5	4·22	259	3·50
	268	3·70	300	2·50		275	3·74	308	2·90
	378	3·73				382	3·76		
3-Chloro- ..	236·	4·08	303	2·94	6-Methoxy-	236	4·15	260	3·28
	258*	3·56				284	3·70	316	2·64
	280*	3·30				393	3·66		
	370	3·34							
					6-Methyl-	228	4·16	255	3·43
3-Methoxy-	232·5	4·02	265	3·14		276	3·74	310	2·71
	290	3·37	320	3·20		382	3·70		
	355·5	3·37							
					6-Nitro-	223	4·43	240	4·08
3-Methyl- ..	234	4·41	270	3·67		249	4·15	289	2·92
	277	3·70	305	3·01		307†	2·98	331	2·81
	376	3·76				408	3·99		
3-Nitro- ..	225·5	4·18	306	2·72					
	262*	3·44							
	379	3·56							

* These are points of inflection.

† This peak is due to overlapping of the broad 408 and 223 mμ peaks

(*h*) *Oxidations of Benzylamine with Iodosobenzene Diacetate*

(i) *Oxidation with Iodosobenzene Diacetate in Benzene Solution.*—The amine (1·00 ml) was oxidized in benzene solution as in Section II (*b*) ; oxidation was complete in 4 days at 19 °C. The solvent was removed by distillation from a water-bath at atmospheric pressure. The oily residue was treated with ethanolic 2,4-dinitrophenylhydrazine, and benzaldehyde 2,4-dinitrophenylhydrazone (1·01 g), m.p. and mixed m.p. 234–235 °C, was filtered off. Only an intractable gum (0·25 g) was isolated from the filtrate.

(ii) *Oxidation with Iodosobenzene Diacetate in Acetic Acid Solution.*—Oxidation of the amine (1·00 ml) was carried out as in Section II (*b*); uptake of 1·1 mol of the oxidant was complete after 5 days at 45 °C. The reaction mixture was distilled from a water-bath at 20 mm; treatment of the distillate with 2,4-dinitrophenylhydrazine precipitated benzaldehyde 2,4-dinitrophenylhydrazone (0·30 g), m.p. and mixed m.p. 233–234 °C. The oily distillation residue (0·83 g) was treated as in Section II (*b*). No products were eluted from the chromatogram. The ethanol extract of the alumina was sublimed and a colourless product (0·17 g) separated at 140 °C/0·2 mm. The sublimate crystallized from light petroleum as colourless, flattened prisms of *N*-benzylacetamide, m.p. and mixed m.p. 59–60 °C.

(*i*) *Ultraviolet Spectra of Substituted-2-nitroanilines*

The spectra were recorded with a Hilger Uvispek spectrophotometer in the range 215–415 mμ. 10^{-4}M solutions of the 2-nitroanilines in *cyclo*hexane were employed; the solvent was purified by the method of Crowe and Smythe (1951). The essential features of the spectra are presented in Table 6.

III. Discussion

(*a*) *Preparation of Amines*

Although most of the amines were prepared by standard procedures, the following compounds were synthesized by new methods.

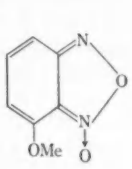
(i) *3-Methoxy-2-nitroaniline.*—This compound (m.p. 124 °C) was prepared by the reaction of (1) 3-methoxy-2-nitrobenzoic acid with sodium azide in concentrated sulphuric acid (Schmidt reaction), and (2) 3-methoxy-2-nitrobenzamide with sodium hypochlorite (Hofmann degradation). It was necessary to carry out the Hofmann degradation in 68 per cent. aqueous *tert.*-butanol since aqueous sodium hypochlorite readily oxidized the intermediate 3-methoxy-2-nitroaniline to 4-methoxybenzofurazan oxide (Ia or Ib). This latter compound was identical with the product of the iodosobenzene diacetate oxidation of 6-methoxy-2-nitroaniline (cf. Green and Rowe 1913; Hammick, Edwardes, and Steiner 1931; Pausacker and Scroggie 1954*b*).

It may be noted that Boyer *et al.* (1955) have recently proposed the alternative formula IIa (and the contributing forms IIb, IIc, etc.) for benzofurazan oxides, although the structure IIa had previously been considered, and rejected, by Green and Rowe (1917), Tappi (1941), Buchmeier and Ruggli (1945), and Gaughran, Kaufman, and Picard (1954). In the present paper, the more generally accepted benzofurazan oxide structure (Ia, Ib) will be preferred although further work may well show the *o*-dinitroso structure is correct.

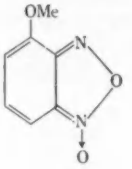
Reverdin and Widmer (1913) have claimed that 3-methoxy-2-nitroacetanilide is formed, in 0·2 per cent. yield, by nitration of 3-methoxyacetanilide; the free base had m.p. 143 °C. This m.p. differs from that reported above. Furthermore, repetition of this nitration under varying conditions has only led to the isolation of 3-methoxy-4-nitroaniline (m.p. 131 °C) and 3-methoxy-2,4-dinitroaniline (m.p. 157 °C). The orientation of substituents in the latter amine was established by examination of the infra-red spectrum.

(ii) *6-Methoxy-2-nitroaniline.*—This compound was prepared by hydrolysis of 6-methoxy-2-nitrobenzonitrile, with alkaline hydrogen peroxide, to 6-methoxy-2-nitrobenzamide, which was then reacted with sodium hypochlorite (Hofmann degradation) in an aqueous *tert.*-butanol solvent. The melting points of the

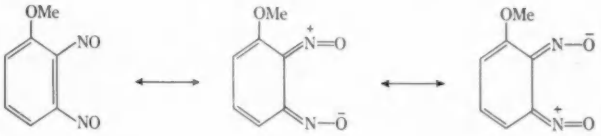
amine, and its acetyl derivative, corresponded to those given by Ingold and Ingold (1928), who prepared the amine by the nitration, and subsequent methylation, of *ON*-diacetyl-2-aminophenol.



(Ia)



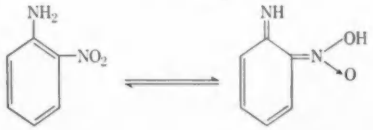
(Ib)



(IIa) (IIb) (IIc)

(b) Oxidation of 3(or 6)-Substituted-2-nitroanilines

(i) *Oxidations with Iodosobenzene Diacetate in Benzene Solution.*—Pausacker and Scroggie (1954*b*) have found that oxidation with iodosobenzene diacetate in benzene solution converts 4- or 5-substituted-2-nitroanilines to the corresponding benzofurazan oxides in excellent yield, while moderate yields of azo compounds are produced in acetic acid solution (Barlin, Pausacker, and Riggs 1954). It was proposed that, in benzene solution, oxidation proceeded via attack by the oxidant on the hydroxyl group of the *aci*-nitro tautomeric form IIIa to form an ester. The tautomeric form IIIa was supposed not to exist in acetic acid solution since this solvent would interfere with the stabilizing intramolecular hydrogen bonding. Oxidation would then proceed by attack on the amino group of III to yield the free radical precursors of azo compounds.

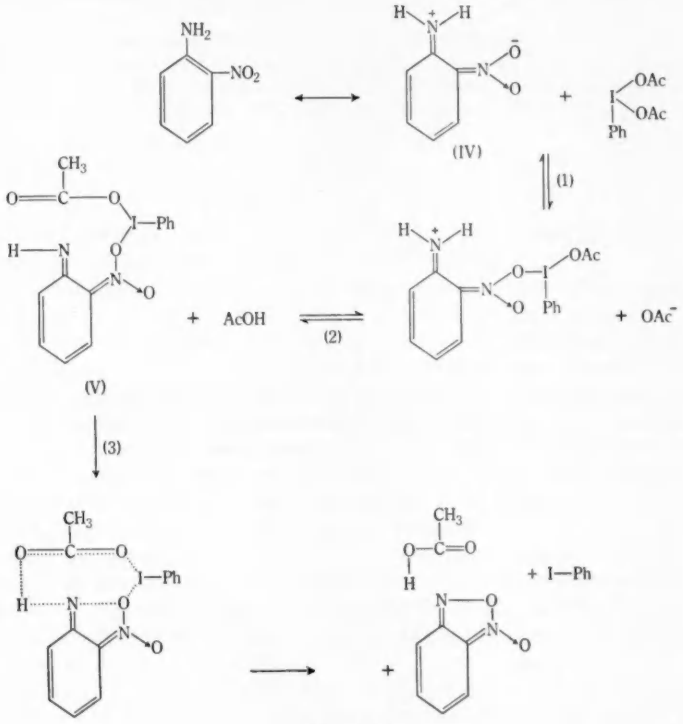


(III) (IIIa)

We now find that, when 3-methyl-2-nitroaniline is oxidized with iodosobenzene diacetate in benzene solution, both the benzofurazan oxide (42 per cent.) and the azo compound (28 per cent.) are produced ; this would imply oxidation of both tautomeric forms of this nitroaniline. Since acetone, like acetic acid, would interfere with the intramolecular hydrogen bonding of the *aci*-nitro tautomer, oxidation of 3-methyl-2-nitroaniline in acetone solution should proceed,

via III, to give a higher yield of the azo compound. A higher yield of the benzofurazan oxide is actually formed in acetone solution, and the reaction is much faster. This would indicate that the *aci*-nitro concept is not correct.

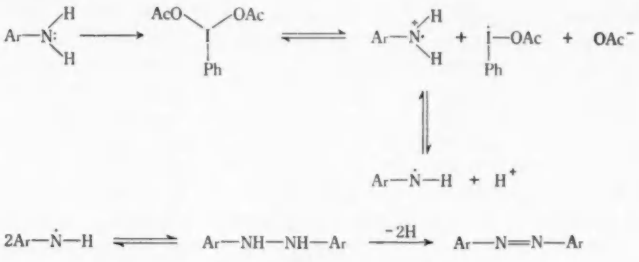
3-Methyl-, 3-methoxy-, and 3-chloro-2-nitroaniline are all oxidized by iodosobenzene diacetate in benzene solution to a mixture of the corresponding benzofurazan oxide and azo compound. By changing the nature of the solvent, the ratio of the yields of benzofurazan oxide and azo compound obtained from



Mechanism 1

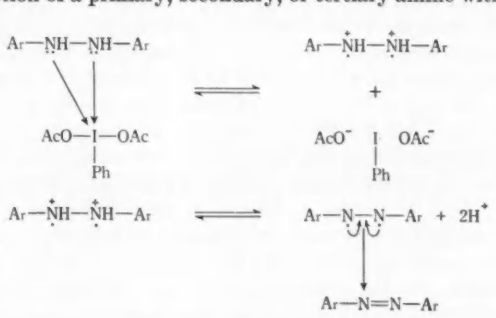
3-methyl-2-nitroaniline could be changed. These results indicate two energetically similar reaction paths by which 2-nitroanilines may be oxidized. We now propose that the reaction involves nucleophilic attack on the trivalent iodine atom of the oxidant. There are two potential nucleophilic centres in the nitroamine molecule—the lone electron pair on the amino nitrogen atom, and the nitro group oxygen atoms of the charged contributing form IV of a 2-nitroaniline—and the identity of the oxidation product will depend on which centre is the more reactive. The two alternative reaction paths are shown (mechanisms 1 and 2). Mechanism 2 is applicable to the oxidation of other substituted anilines.

The final stage of mechanism 2 is acceptable since hydrazobenzene is oxidized to azobenzene in 92 per cent. yield with iodosobenzene diacetate in benzene solution (Pausacker 1953). It is possible that this stage of the oxidation proceeds via mechanism 3, although the PhIOAc radical produced in mechanism 2 may also play a part.



Mechanism 2

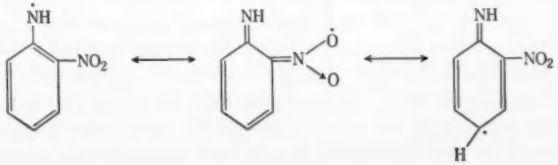
There are no decisive reasons why the nucleophilic attack in mechanism 2 leads to formation of two free radicals instead of an *N*-ester, though the N-I(III) bond has yet to be observed. The most satisfactory feature of this mechanism is that the reaction of a primary, secondary, or tertiary amine with iodosobenzene



Mechanism 3

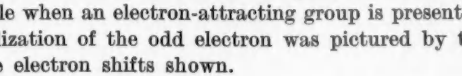
diacetate involves nucleophilic attack by the amino-nitrogen lone pair of electrons on trivalent iodine as the first stage. The reactions of *N*-substituted-anilines with this oxidant have been described by Mitchell and Pausacker (1957).

The radical ArNH· has several contributing forms, for example, VIa, VIb, VIc, etc.



(VIa) (VIb) (VIc)

and only symmetrical coupling of the form VIa would lead to azo compound formation. Hughes and Saunders (1954) have pointed out that the form ArNH· will be most stable when an electron-attracting group is present in the aromatic nucleus. Delocalization of the odd electron was pictured by these authors as occurring via the electron shifts shown.



(VIIa) (VIIb)

In agreement with this theory it has already been shown that yields of azo compounds obtained by oxidation of substituted-anilines with iodosobenzene diacetate in benzene solution are highest when the substituents are electron-attracting (Pausacker 1953). Although Hughes and Saunders included 4-fluoro-aniline within this scheme, it must be pointed out that fluorine cannot accommodate the nine electrons required by VIIb.

In mechanism 1, steps (1) and (2) must be reversible since 4-nitroaniline should undergo them, though the later steps would not be possible. The later steps of the mechanism are the same as those proposed by Pausacker and Scroggie (1954*b*). Furthermore, this mechanism is in accord with the kinetic results recently obtained by Pausacker and Scroggie (1958). The "intermediate" proposed by these workers would therefore be represented by structure V. It is evident from the overall mechanism that *N*-substituted-2-nitroanilines cannot be oxidized to benzofurazan oxides. We have previously claimed (Pausacker and Scroggie 1954*b*) that the failure of 2-nitroacetanilide and *N*-methyl-2-nitroaniline to react with iodosobenzene diacetate, in benzene solution at room temperatures, is attributable to the only amino hydrogen atom being rendered inert to oxidation by intramolecular hydrogen bonding. Dyall and Hambly (1958) have found that 2-nitroacetanilide is bonded in this way, but found no evidence for intramolecular hydrogen bonding in 2-nitroaniline. It is therefore most unlikely that such bonding would be found in *N*-methyl-2-nitroaniline, as the amino hydrogen atom in this compound would be less acidic than those in 2-nitroaniline. If mechanism 2 is correct, the lack of reactivity of 2-nitro-acetanilide is presumably due to delocalization of the amino nitrogen lone pair of electrons by the acetyl group. The failure of *N*-methyl-2-nitroaniline to react by mechanism 2 is surprising, but may be due to shielding of the lone pair by the methyl and nitro groups. No attempt was made by Pausacker and Scroggie (1954*b*) to oxidize this compound at temperatures higher than 20 °C.

In 2-nitroaniline, the development of negative charges on the nitro group oxygen atoms is accompanied by delocalization of the amino nitrogen electron pair, and mechanism 1 is accordingly followed exclusively. Only in instances where conjugation of the nitro group with the aromatic ring is reduced is it probable that the two nucleophilic centres would have comparable nucleophilic reactivities. Nitro group conjugation in the 4- or 5-substituted-2-nitroanilines should be comparable with that in 2-nitroaniline, and accordingly oxidation follows mechanism 1. An exception is provided by 4-methoxy-2-nitroaniline,

whose oxidation yielded 5 per cent. of the azo compound as the only identifiable product (Pausacker and Scroggie 1954*b*). The infra-red spectrum of this amine (Dyall and Hambly 1958) clearly indicates high electron density on the amino nitrogen atom, due to the $+M$ effect of the *para*-methoxy group. Oxidation of this amine via mechanism 2 is not therefore surprising.

Studies of the ultraviolet spectra of alkyl substituted-4-nitroanilines by Wepster (1957) indicate that, despite nitro-amino conjugation, the nitro group (but not the amino group) is rotated out of the plane of the aromatic ring by an *ortho*-methyl group. This result is supported by the dipole moments of *ortho*-substituted nitrobenzenes (Birtles and Hampson 1937 ; Hampson and Ingham 1939). This rotation of the nitro group will be accompanied by lower development of charge on the nitro group oxygen atoms. The N-O stretching frequencies in the infra-red should thus be raised, and the intensities of these absorptions be lowered, in comparison with instances where there is no steric inhibition of conjugation. Actually, only the symmetric N-O stretching motion is affected (van Veen, Verkade, and Wepster 1957 ; Dyall and Hambly 1958). The infra-red spectra of 3-substituted-2-nitroanilines have been studied by Dyall and Hambly (1958), but the elevation of the symmetric N-O stretching frequency, which should accompany reduced conjugation, could not be observed. Two strong absorptions occurred in the 1315–1365 cm^{-1} region, and a reliable identification could not be made. However, the extinction coefficients of these motions were lower than for 2-nitroaniline. van Veen, Verkade, and Wepster (1957) report that one unbranched alkyl group *ortho* to an aromatic nitro group does not affect the symmetric N-O stretching frequency, and the extinction coefficient data (Dyall and Hambly 1958) is probably the only indication of reduced nitro group conjugation which can be obtained from the infra-red spectra. Moreover, in the spectra of the 3-substituted-2-nitroanilines, the extinction coefficients of both N-H stretching motions, and the frequencies of the asymmetric N-H stretching motion, are lowered with respect to 2-nitroaniline, and these results are expected if nitro-amino conjugation is reduced. The ultraviolet spectra of the eight 3- or 6-substituted-2-nitroanilines (Table 6) did not provide definite information on the extent of conjugation ; the positions and intensities of the 230 and 260 mμ absorptions were affected by mutual overlapping. The 260 mμ absorptions in the spectra of the two methoxy-substituted-2-nitroanilines also included absorption by the aromatic methoxyl system, to judge by their asymmetric shape. The 360 mμ nitro group absorption was also not particularly informative. However, the weak maximum at short wavelengths in the spectrum of 3-methoxy-2-nitroaniline clearly indicates reduced nitro group conjugation. The long wavelength maximum in the ultraviolet spectrum of 2,6-dinitroaniline indicates coplanarity with the aromatic ring, though the extinction coefficient is low for a molecule with two equivalent nitro groups ; this indicates a low probability of both nitro groups simultaneously becoming charged in the excited state.

Steric inhibition of nitro group conjugation will be accompanied by lowered nucleophilic reactivity of the nitro group oxygen atoms, and (since the extent of delocalization of the amino nitrogen lone electron pair will be lessened) by

increased nucleophilic reactivity of this latter centre. Hence it is possible for the 3-substituted-2-nitroanilines to be oxidized by both mechanisms 1 and 2, to yield both benzofurazan oxides and azo compounds. It is reasonable to assume that steric effects in the transition state parallel those detected in the ground state by both spectral and dipole moment measurements.

It does not necessarily follow that the presence of a 3-substituent in a 2-nitroaniline will result in azo compound formation. If the 3-substituent exerts an overall electron-withdrawing effect, the resultant delocalization of the amino nitrogen lone pair of electrons will reduce the nucleophilic reactivity of this centre. Consequently, mechanism 1 predominates in the oxidation of 3-chloro-2-nitroaniline, and is followed exclusively in the oxidation of 2,3-dinitroaniline.

The oxidations of 3-methyl-2-nitroaniline in various solvents also follow a pattern predicted from simultaneous operation of mechanisms 1 and 2. In acetone solution, N—H $\cdots$ O=C intermolecular hydrogen bonds are formed between the amino group and the solvent molecules (Dyall and Hambly 1958). The nucleophilic amino group will thus be shielded, and its reactivity will be lowered. Mechanism 1 is accordingly more favoured in this solvent than in benzene. Dyall and Hambly (1958) have found no evidence for hydrogen bond formation between 3-methyl-2-nitroaniline and chlorobenzene, although interaction between the aromatic π-electrons of these two compounds was detected. The effect of this interaction on the oxidation cannot be predicted. In acetonitrile there would be no shielding effect due to intermolecular hydrogen bonding. The extensive formation of high molecular weight materials suggests that the free radical intermediates in mechanism 2 attack the α-hydrogen atoms of the solvent.

In mechanism 1, IV can be hydrogen bonded with acetone due to the acidity of the hydrogens on the $=NH_2^+$ group. It is improbable that hydrogen-bonded solvation of the uncharged =NH group in V by acetone would be sufficiently marked to prevent formation of the cyclic transition state.

The oxidation of 2-nitro-1-naphthylamine in acetone yields naphthofurazan oxide (9 per cent.) only, although it has been shown that both naphthofurazan oxide (7 per cent.) and azo compound (3 per cent.) are formed in benzene solution (Pausacker and Scroggie 1954*b*). In both solvents, the remaining amine was converted to an intractable mixture of materials of high molecular weight. Oxidation of 1-nitro-2-naphthylamine in benzene solution yields 86 per cent. naphthofurazan oxide and 3 per cent. azo compound (Pausacker and Scroggie 1954*b*), and this difference in behaviour of these two amines on oxidation has been explained on the basis of the differing stabilities of the free radicals formed by homolytic fission of the amine-oxidant ester. If the amino group in 2-nitro-1-naphthylamine is more nucleophilic than that in 1-nitro-2-naphthylamine, however, these results could now be explained on the basis that the former compound is more likely to oxidize via mechanism 2. Bryson (1949) has measured the basicities of these two compounds in aqueous solutions, and found that 2-nitro-1-naphthylamine is actually the slightly weaker base. This does not mean that the above hypothesis must be discarded, since nucleophilic properties

in benzene solution cannot be directly correlated with basicities in aqueous solution. Moreover, the large amount of intractable material formed from 2-nitro-1-naphthylamine may be produced by a reaction path other than those shown in mechanisms 1 and 2, in which case the relative importance of these two mechanisms cannot be evaluated.

The behaviour of 2,6-dinitroaniline and 6-chloro-2-nitroaniline towards oxidation can be interpreted by consideration of their infra-red spectra (Dyall and Hambly 1958). The extinction coefficients of the N-O stretching motions in 2,6-dinitroaniline are very low for a compound with two equivalent nitro groups. This indicates that the charges on the nitro groups are not strongly developed, and this result is not surprising since both nitro groups are conjugated with the one amino group. Although the nucleophilic reactivity of the nitro groups is therefore low, oxidation via mechanism 2 is not possible as the strong $-I$, $-M$ effects of the two nitro groups would cause extensive delocalization of the amino group lone pair of electrons. Slow oxidation via mechanism 1 is therefore observed. The alternative explanation of the low extinction coefficients in the infra-red is that the nitro groups do not lie in the plane of the aromatic ring and therefore are not fully conjugated. This would, however, be clearly evident by a weak nitro group absorption in the ultraviolet spectrum, at a shorter wavelength than in 2-nitroaniline; actually the maximum in the spectrum of 2,6-dinitroaniline is in the other direction. A similar lowering of extinction coefficients is evident in the infra-red spectrum of 1,3-dinitrobenzene, where once again two nitro groups are withdrawing electrons from the same source. 6-Chloro-2-nitroaniline is similar to 2,6-dinitroaniline in that the electron-withdrawing power of its nitro group is opposed by the overall electron-withdrawing effect of the chloro substituent; oxidation via mechanism 2 is prevented by delocalization of the amino group lone electron pair and only slow oxidation to the benzofurazan oxide is possible.

6-Methoxy-2-nitroaniline yields only 2 per cent. benzofurazan oxide, and the benzofurazan oxide cannot be isolated from the reaction with 6-methyl-2-nitroaniline. Neither amine yields any azo compound under these conditions, and, since 6-methyl-2-nitroaniline does yield the azo compound on oxidation with lead tetra-acetate in benzene solution, it is improbable that ArNH· radicals are involved. The infra-red spectra of these two nitroanilines are very similar to that of 2-nitroaniline (though the extinction coefficients for their N-O stretching motions are slightly lower), and there are no significant features in their ultraviolet spectra. The spectral studies thus reveal no significant steric interactions in the ground state, but it is possible that steric effects in the transition states of mechanisms 1 and 2 do operate against oxidation via these reaction routes. A different mechanism, or mechanisms, may therefore operate in the oxidation of these two amines. In the case of 6-methoxy-2-nitroaniline, it is possible that the methoxyl group lone electrons attack the oxidant, as it has been noted previously that the oxidation of methoxy- and ethoxyanilines with iodosobenzene diacetate in benzene solution produces chiefly uncharacterizable materials (Pausacker 1953; Mitchell and Pausacker 1954).

(ii) *Oxidations with Iodosobenzene Diacetate in Acetic Acid Solution.*—The failure to obtain benzofurazan oxides in this solvent can be ascribed to strong solvation of the feebly-basic imino group of the ester V by acetic acid molecules; the presence of a strongly held solvation shell would prevent formation of the cyclic complex. Similar solvation of the amino group would reduce its nucleophilic reactivity, so that mechanism 2 would not easily be followed. This interpretation is supported by the work of Barlin, Pausacker, and Riggs (1954), who noted that aromatic amines which yield azo compounds on oxidation with iodosobenzene diacetate in benzene solution are almost invariably oxidized to a lower yield of azo compound in acetic acid solution. In the present work, the 6-substituted-2-nitroanilines did not yield azo compounds, possibly because the amino nitrogen lone pair is shielded, not only by the solvation shell, but also by the two *ortho*-substituents. The feeble basicity of two of these compounds, already discussed, would also render mechanism 2 an unfavourable reaction path. 2,3-Dinitroaniline is likewise only very feebly basic, and yields no azo compound, but the other three 3-substituted-2-nitroanilines give low yields of azo compounds.

The high yields of intractable mixtures which form in these oxidations, even when no azo compound is isolated, indicate that mechanisms 1 and 2 are not the only routes which the oxidation may follow.

The isolation of the *N*-acetyl derivative of 3-methyl-2-nitroaniline does not indicate ability of the oxidant to function as an acetylating agent, since it was shown that this amine is partly acetylated on prolonged contact with acetic acid.

(iii) *Oxidations with Lead Tetra-acetate.*—Of all the oxidation methods tested in this work, use of lead tetra-acetate in benzene solution was the most successful for preparing azo compounds. No azo compound was obtained from 6-methoxy-2-nitroaniline, which was converted into intractable mixtures, or from 2,6-dinitroaniline, which was recovered quantitatively. The latter amine apparently catalyses decomposition of the oxidant, since the oxidant titre in its presence decreased much more rapidly than the oxidant titre of a solution of lead tetra-acetate in benzene, maintained under identical reaction conditions.

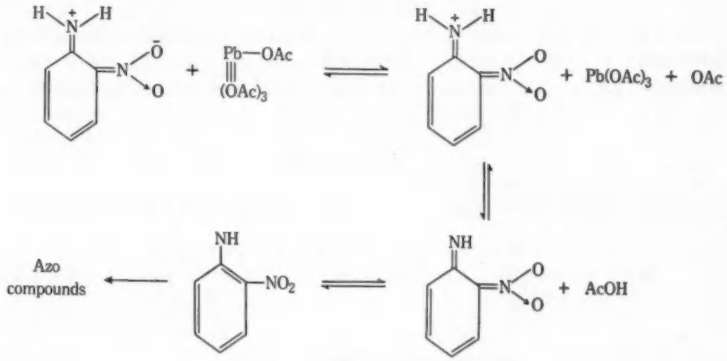
In the oxidations yielding azo compounds, the charged form of the nitroamine is presumably the active nucleophile in most instances. The failure to obtain benzofurazan oxides in benzene solution indicates, however, that ester formation with the oxidant does not occur. The formation of azo compounds suggests that the attack on the oxidant leads to formation of two free radicals (mechanism 4).

The subsequent reactions of the ArNH radicals have already been discussed, and it is known that, in acetic acid solution, lead tetra-acetate oxidizes hydrazobenzene to azobenzene in 95 per cent. yield (Pausacker and Scroggie 1954*a*).

The failure of the nitroamine and oxidant to form an ester may be due to the small radius (0·85 A) of Pb(IV) (Evans 1939), compared with that of I(III), which, lying between I and I(V) would have an ionic radius of approximately 1·15 A. The Pb(IV) atom may not be able to accommodate the five groups in the transition state of the nucleophilic attack by the nitroamine, so that homolytic breakdown in the transition state occurs.

Mechanism 4 presumably operates in both benzene and acetic acid solutions. In acetic acid solution, however, the $Pb(OAc)_3$ radical is likely to attack the solvent instead of taking part in further oxidation of the amine. This may account for the proportion of the amine recovered from oxidations in this solvent usually being higher than from oxidations in benzene solution.

A mechanism analogous to mechanism 2 must operate when many types of aromatic amines are oxidized to azo compounds with lead tetra-acetate. Even in the oxidation of 2-nitroanilines the possibility of the nucleophilic centre being the amino nitrogen lone electron pair cannot be excluded, particularly for several of the 3-substituted-2-nitroanilines.



Mechanism 4

(iv) *Oxidations with Alkaline Sodium Hypochlorite.*—Green and Rowe's (1912) mechanism for the oxidation of 2-nitroanilines to benzofurazan oxides with alkaline sodium hypochlorite is stoichiometric rather than being descriptive of mechanism, and our studies do not appear to assist in the elucidation of this mechanism. The oxidations of 2,3- and 2,6-dinitroaniline with sodium hypochlorite in alkaline ethanol are complicated by chlorination, and the isolation of X-chloro-4-ethoxybenzofurazan oxide from the reaction with 2,3-dinitroaniline indicates that nucleophilic replacement of a nitro group can also occur under these conditions. It should be noted that a small amount of the azo compound, in addition to the benzofurazan oxide, is formed from the oxidation of 6-methyl-2-nitroaniline. Azo compounds have been previously obtained from hypochlorite oxidations only when the medium was neutral.

(c) *Oxidations of Benzylamine*

Benzylamine is considerably more basic than any of the 2-nitroanilines, and high nucleophilic reactivity towards iodosobenzene diacetate would be predicted. Thus, according to mechanism 2, the intermediate formation of the benzylamino radical (VII) would be expected.

$$PhI(OAc)_2 + PhCH_2NH_2 \rightarrow PhCH_2\dot{N}H + Ph\dot{I}OAc + AcOH.$$
(VII)

Radical VII may then react, in part, with the PhIOAc radical to form benzaldimine, which is later hydrolysed to benzaldehyde. This reaction shows formal analogies with the Sommelet reaction whereby benzylamine can be oxidized to benzaldehyde in 66 per cent. yield (Angyal *et al.* 1949; Angyal and Rassack 1949; Angyal 1954). The yield of 39 per cent. benzaldehyde obtained by oxidation with iodosobenzene diacetate in benzene solution does not compare favourably from a preparative point of view, though we have not searched for optimum conditions. In acetic acid solution, the amine was extensively acetylated by the solvent, and only an 11 per cent. yield of benzaldehyde was produced.

IV. Acknowledgments

One of us (L.K.D.) wishes to thank the University of Melbourne for a Research Grant (1956), and the Dunlop Rubber Company of Australia for a Research Scholarship (1957). Discussions with Associate-Professor A. N. Hambly were of the greatest value.

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REACTIONS OF AROYL PEROXIDES*

V. BENZOYL PEROXIDE WITH FERROCENE

By K. H. PAUSACKER†

[*Manuscript received June 2, 1958*]

Summary

When ferrocene reacts with varying amounts of benzoyl peroxide in benzene solution, the iron in ferrocene is almost completely converted into ferric benzoate. The additional benzoyl peroxide apparently reacts with the *cyclo*pentadienyl fragments forming benzoic acid and intractable material.

As neither carbon dioxide nor diphenyl could be isolated from the reaction mixture, it would appear that ferrocene acts as an efficient " scavenger " for benzoyloxy radicals.

I. INTRODUCTION

Fenton's reagent (ferrous sulphate-hydrogen peroxide) has proved to be a useful oxidant for certain organic compounds which are soluble in water. It was desired to find a reagent which is soluble in common organic media in order to extend the range of this type of oxidation and the first system chosen was ferrocene-benzoyl peroxide. It is already known that Fenton's reagent reacts with benzene forming phenol and diphenyl (Merz and Waters 1949; Baxendale and Magee 1953) and so the reaction of benzene with ferrocene-benzoyl peroxide was studied both for comparative purposes with Fenton's reagent and in order to see if benzene would serve as a suitable solvent for other oxidations.

II. EXPERIMENTAL

Analyses were made by the C.S.I.R.O. Microanalytical Laboratory.

Ferrocene (1·88 g; 0·010 mol) was refluxed with benzoyl peroxide (0·010, 0·015, and 0·020 mol) in benzene (50 ml) for 7 hr. When the reagents were mixed, the solution turned green initially and heat was evolved. Shortly after refluxing began, the solution became brown and a buff-coloured precipitate began to form. The cooled reaction mixture was filtered and the solid was washed with benzene (3×10 ml). The red-brown solid proved to be ferric benzoate (Found: C, 60·6; H, 4·0%. Calc. for $C_{21}H_{15}O_6Fe$: C, 59·9; H, 3·6%). It dissolved in warm dilute sulphuric acid and the theoretical amount of benzoic acid was obtained by ether extraction. The remaining aqueous solution was treated with ammonia and ferric hydroxide precipitated. When this was filtered and ignited, the expected quantity of ferric oxide was obtained.

* For Part IV of this series see *Aust. J. Chem.* **11**: 336.

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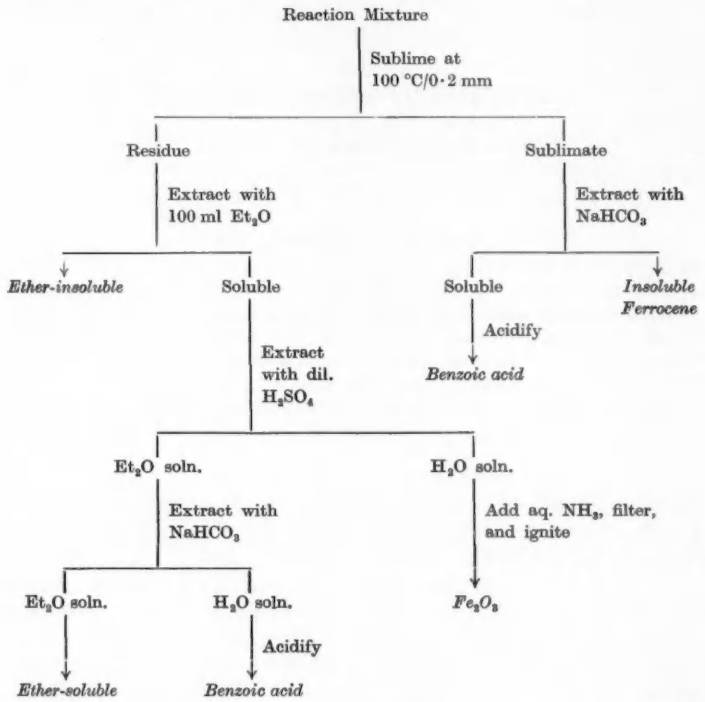
The benzene solution was evaporated on the water-bath and the residue was treated as shown in the following flow sheet:



Benzoic acid and ferrocene were identified by mixed m.p. with authentic specimens. The dark brown, ether-insoluble fraction contained some ferric benzoate as both benzoic acid and ferric oxide could be obtained after treatment with dilute sulphuric acid. A portion of this fraction was ignited and the residue was assumed to be ferric oxide resulting from ferric benzoate. Independent experiments showed that ferric benzoate gave the theoretical yield of ferric oxide when ignited.

The results are shown in Table 1, allowance being made for the ferric benzoate assumed to be in the ether-insoluble fraction. The presence of diphenyl could not be detected.

Ferrocene (2 g), benzoyl peroxide (7 g), and benzene (200 ml) were heated at 78 °C, in an atmosphere of carbon dioxide, in a closed vessel connected to a gas-measuring apparatus. No gas evolution was observed.

The reaction can also take place slowly at room temperature for a mixture of ferrocene (0·010 mol), benzoyl peroxide (0·010 mol), and benzene (100 ml) deposited ferric benzoate (0·50 mol) after standing for 2 months. Ferric benzoate (0·58 mol) was also obtained when 0·015 mol benzoyl peroxide was used.

III. Discussion

Unlike Fenton's reagent, ferrocene-benzoyl peroxide does not appear to react with benzene. Furthermore, the normal reaction of benzoyl peroxide with benzene (Lynch and Pausacker 1957) is inhibited as neither carbon dioxide nor diphenyl was formed.

The reaction occurs exclusively between ferrocene and benzoyl peroxide and the principal product is ferric benzoate. Benzoyl peroxide is not acting in its normal role of a phenylating agent and it may be noted that it has been stated (Pauson 1954 ; Broadhead and Pauson 1955) that ferrocene does not react with benzoyl peroxide and phenylazotriphenylmethane although it is readily phenylated with diazonium salts and *N*-nitrosoacetanilide.

Table 1

REACTION OF BENZOYL PEROXIDE WITH FERROCENE

Quantities are expressed in terms of mol per mol of ferrocene

$(PhCO_2)_2$	1·00	1·50	2·00
Ferrocene recovered ..	0·48	0·39	0·26
Ferric benzoate ..	0·42	0·51	0·72
$PhCO_2H$	0·78	1·05	1·40
Fe_2O_3	0·03	0·02	0·01
Ether-insoluble (g) ..	0·581	1·034	1·319
Ether-soluble (g) ..	0·419	0·706	0·719

As the sum of the molar yields of ferric benzoate and unchanged ferrocene vary between 0·90 and 0·98 (see Table 1), it would appear that almost every mol of reacted ferrocene yields 1 mol of ferric benzoate.

$$Fe(C_5H_5)_2+1\cdot5(PhCO_2)_2\rightarrow Fe(OCOPh)_3+2C_5H_5. \quad \ldots\ldots (1)$$

The *cyclo*pentadienyl fragments apparently react with further benzoyl peroxide (or benzoyloxy radicals) to form benzoic acid and high molecular weight material (ether-insoluble material). Some benzoyloxylation also takes place, particularly at the higher concentrations of benzoyl peroxide, as only 86–89 per cent. of the benzoyloxy radicals are accounted for when 1·50 and 2·00 mol of benzoyl peroxide are used.

Equation (1) is not intended to represent the mechanism of the reaction as some reaction between the *cyclo*pentadienyl fragments and benzoyl peroxide may occur in the original ferrocene molecule, but it is apparent that ferrocene reacts as a very effective " scavenger " for benzoyloxy radicals as no carbon dioxide was liberated during the reaction. Cherniak *et al.* (1958) have recently shown that ferric chloride can also act as a radical scavenger.

Ferrocene is normally regarded as being reasonably stable and fission under the gentle conditions used in this work was unexpected. However, it is known that it can be converted to ferric sulphate by heating with nitric acid-sulphuric acid (Rochow, Hurd, and Lewis 1957) and Trifan and Nicholas (1957) have reported that it can be split by lithium in ethylamine even though it is resistant

to catalytic hydrogenation. It is possible that the molecule of ferrocene itself is not actually split but rather that it is first converted into a ferricinium salt which undergoes the fission reaction. Ferrocene is readily oxidized to ferricinium salts by many oxidizing reagents (Pauson 1955), and the colour changes observed during the reaction indicate that this possibility should not be neglected.

It is interesting to note that the ferrocene-benzoyl peroxide-benzoin system catalyses the polymerization of styrene in almost the same way as the ferric benzoate-benzoyl peroxide-benzoin system (Kern, Achon-Samblancat, and Schulz 1957). These results are readily explained when it is realized that ferric benzoate is formed from ferrocene and benzoyl peroxide.

IV. Acknowledgment

We should like to thank the Linde Air Products Co. for a generous gift of ferrocene.

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HYDROGEN BONDING IN ORGANIC COMPOUNDS

I. *o*-NITROANILINES*

By L. K. DYALL† and A. N. HAMBLY†

[*Manuscript received June* 30, 1958]

Summary

The infra-red spectra of *o*-nitroanilines do not indicate any intramolecular hydrogen bonding unless there are nitro groups in both positions 2 and 6 to the amino group. An examination of the literature shows that there is no unambiguous evidence from other sources of such bonding in simple *o*-nitroanilines. An explanation is given of the variation of the stretching frequencies of the nitro group in sterically hindered compounds and in those with electron-donating *ortho*- and *para*-substituents.

I. INTRODUCTION

In a study being made by one of us (L.K.D.) of the oxidation of nitroanilines, it became important to know the extent to which intramolecular hydrogen bonding was modifying the reactivity of *o*-nitroanilines. If one assumes a length of 1·39 Å for the aromatic C–C bond, that the nitro group is coplanar with the benzene ring, and that the C–N and N–O distances are equal to those found by Abrahams and Robertson (1948) for *p*-nitroaniline, then the distance between the amine nitrogen and the nearer oxygen atom is 2·40 Å. This, according to the formula of Pimentel and Sederholm (1956), should produce a very strong, intramolecular hydrogen bond, with a displacement of the N–H infra-red stretching bands of about 400 cm^{-1} to lower frequencies compared to the frequencies found in isomeric molecules in which such bonding cannot occur. As this promised to be a sensitive method for determining different strengths of hydrogen bonding we decided to measure the spectra of a group of nitroanilines and related compounds in the region 3600–1250 cm^{-1}.

There are only two previous studies of the infra-red spectra of *o*-nitroanilines. Francel (1952) observed the variation of intensity of the NH_2 and NO_2 stretching vibrations in an oriented, crystalline film of *o*-nitroaniline with change in the plane of polarization of the incident radiation. Since these absorptions increased in intensity when the intensity of the bands due to the "out of plane" C–H vibrations decreased, he concluded that both NH_2 and NO_2 were coplanar with the ring. Hathway and Flett (1948) examined the spectra of some nitronaphthylamines and deduced that intramolecular hydrogen bonding occurred in 2-nitro-1-naphthylamine and in 1-nitro-2-naphthylamine.

* A brief report of some of the N–H stretching frequencies in nitroanilines has been published previously by Dyall and Hambly (1958).

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II. Experimental

(*a*) *Apparatus*

The spectra were recorded with a Perkin-Elmer Model 112, single-beam, double-pass, infra-red spectrometer with a fluorite prism. The instrument was calibrated by means of the 2·6 and 6 μ water bands and the spectra of hydrogen chloride and carbon monoxide. These were fitted to two McKinney-Friedel (1948) equations for the ranges 4000–2600 and 2200–1200 cm^{-1} which reproduced the calibration frequencies to ± 1 cm^{-1} in the former region and $\pm 0 \cdot 3$ cm^{-1} in the latter region. Measurements of the broader absorption bands of solutions and solids were reproducible to ± 2 at 3500 cm^{-1} and to ± 1 at 1500 cm^{-1}. Intensities were measured as extinction coefficients at the absorption maximum, using concentrations determined from the known weight of solute dissolved in a given volume of solvent, or by evaporation of a known volume of saturated solution. The optical densities were measured directly from recorder charts of the spectrum of the solution and the pure solvent. The reproducibility was poor, *c.* ± 10 per cent. in $\varepsilon_{max.}$ for solutions of different concentrations. Intensities measured in this way change with slit-width. This was 5–6 cm^{-1} for the N–H stretching region and 1–2 cm^{-1} for the 1700–1200 cm^{-1} region. Solutions were examined in cells of thickness 0·095 and 0·319 mm with sodium chloride windows, except for a few very sparingly soluble compounds for which the N–H stretching frequencies were studied in saturated solutions in 10·0 mm cells with silica end-plates.

(*b*) *Materials*

Melting points are corrected. "Light petroleum" was a fraction b.p. 55–97 °C.

Aniline and 2,6-dimethylnitrobenzene were commercial samples which were distilled, and middle fractions separated, immediately before use.

Nitrobenzene (B.D.H.) was washed successively with alkali and water, dried over calcium chloride, and twice distilled with reservation of the middle fraction, b.p. 51 °C/0·1 mm; $n_D^{18} = 1 \cdot 554$.

1,2-Dinitrobenzene was twice recrystallized from water and dried over phosphorus pentoxide, m.p. 117·5–118·5 °C.

1,3-Dinitrobenzene was twice recrystallized from ethanol and dried over phosphorus pentoxide, m.p. 90–91 °C.

2-Nitroaniline (B.D.H. laboratory reagent) was twice recrystallized from distilled water and after drying over phosphorus pentoxide had m.p. 72·0–72·5 °C.

NN-Dideutero-2-nitroaniline was prepared by treating 0·1 g of 2-nitroaniline *in vacuo* with three successive 1 ml portions of 99·6 per cent. deuterium oxide. The dried sample was handled subsequently in a dry box, but, owing to incomplete wetting by the deuterium oxide, only partial deuteration was obtained.

3-Nitroaniline, m.p. 114·0–114·5 °C and 4-nitroaniline, m.p. 147·0–147·5 °C, were recrystallized from dry, thiophene-free benzene.

3-Chloro-2-nitroaniline was prepared by the acid catalysed rearrangement of 3-chlorophenylnitramine (Dyall and Pausacker 1958). It recrystallized as fine yellow needles, m.p. 108·0–108·5 °C, from benzene-light petroleum.

3-Methoxy-2-nitroaniline was prepared by the Schmidt degradation from 3-methoxy-2-nitrobenzoic acid (Ewins 1912) and by the Hofmann degradation of 3-methoxy-2-nitrobenzamide (Dyall and Pausacker 1958). The amine recrystallized from light petroleum as fine yellow needles, m.p. 124·0–124·5 °C.

3-Methyl-2-nitroaniline was obtained by reduction of 2,3-dinitrotoluene with stannous chloride (Burton and Kenner 1921) and crystallized from benzene-light petroleum as fine orange needles, m.p. 107·0–107·5 °C.

2,3-Dinitroaniline was prepared from 3-nitroacetanilide by nitration (Bendich and Kremer 1939) and subsequent hydrolysis of the acetyl derivative (Pausacker and Scroggie 1955). The product crystallized from benzene as yellow needles, m.p. 128·5–129·0 °C.

6-Chloro-2-nitroaniline was obtained from 2,3-dichloronitrobenzene by ammonolysis under pressure (Lobry de Bruyn 1917) and crystallized from light petroleum as bright yellow needles, m.p. 73·5–74·0 °C.

6-Methoxy-2-nitroaniline was prepared from 6-methoxy-2-nitrobenzonitrile (Organic Syntheses 1942). The nitrile was hydrolysed to the corresponding acid which was then converted to the amide. Hofmann degradation of the latter produced the desired amine (Dyall and Pausacker 1958); fine, orange needles, m.p. 75·5–76·0 °C, from light petroleum.

6-Methyl-2-nitroaniline, prepared from aceto-*o*-toluidide by nitration followed by hydrolysis (Cohen and Dakin 1901), crystallized from light petroleum as long orange rods, m.p. 96·5–97·0 °C.

2,6-Dinitroaniline, obtained by the method of Hegedüs (1950) from chlorobenzene, crystallized from benzene (charcoal) as bright yellow, flattened needles, m.p. 141·5–142·0 °C.

2,4,6-Trinitroaniline was prepared by the nitration of 4-nitroaniline (Holleman 1930), and crystallized from benzene as flattened, yellow needles, m.p. 191·0–191·5 °C.

2-Nitroacetanilide and 4-nitroacetanilide were of B.D.H. laboratory reagent grade and were used without further purification.

Purified samples of 2,4-dinitroaniline, m.p. 180–181 °C; 4-methoxy-2-nitroaniline, m.p. 129–130 °C; *NN*-dimethyl-4-nitroaniline, m.p. 162·0–162·5 °C; 1-nitro-2-naphthylamine, m.p. 126–127 °C; and 2-nitro-1-naphthylamine, m.p. 143·0–143·5 °C, were supplied by Dr. K. H. Pausacker.

Carbon tetrachloride was of B.D.H. spectroscopic grade, dried over anhydrous sodium sulphate, and fractionated through an all-glass Widmer column; b.p. 76·6 °C/755 mm, $n_D^{18}=1\cdot461$.

Chloroform was washed with concentrated sulphuric acid and water, dried over anhydrous sodium sulphate, and fractionated; b.p. 61·0 °C/758 mm.

Tetrachloroethylene (Imperial Chemical Industries, B.P. grade) was washed with water, dried over anhydrous calcium chloride, and fractionated, b.p. 112 °C/758 mm.

Acetone was purified with potassium permanganate and distilled from freshly dehydrated potassium carbonate (Weissberger 1955), b.p. 55·9 °C/757 mm, $n_D^{15}=1\cdot360$.

III. Results and Discussions

(*a*) *Stretching Frequencies of NH Bonds in Non-Polar Solvents*

The stretching frequencies of the NH bonds appear as two bands of moderate intensity in the region 3300–3525 cm^{-1} for dilute solutions of the various primary amines in non-polar solvents such as carbon tetrachloride or tetrachloroethylene. The corresponding bands of hydroxylic compounds show a decrease in intensity as the solutions become more concentrated while new bands of increasing intensity, due to intermolecular hydrogen bonding, appear at lower frequency. The

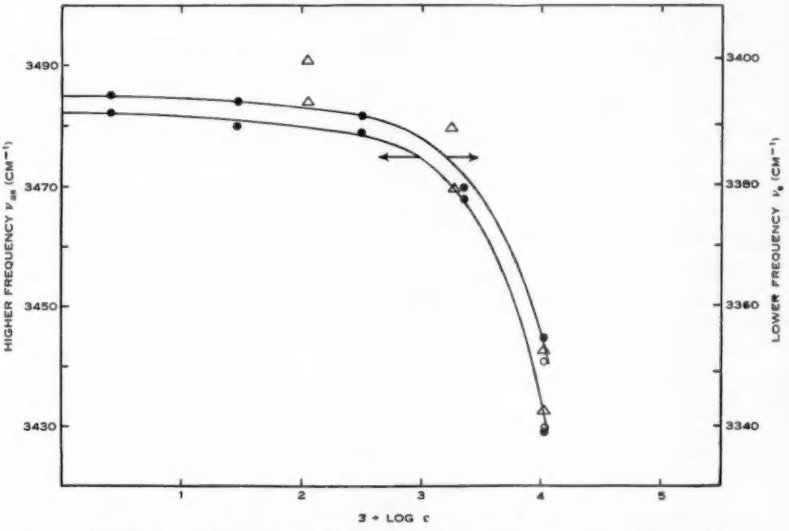


Fig. 1.—Variation of N–H stretching frequencies of aniline with concentration. Solutions in C_2Cl_4 or CCl_4.

○ Califano and Moccia (1957); △ Richtering (1956); ● Present work.

amines on the other hand show only a steady displacement to lower frequency with broadening of the bands as the solutions become more concentrated. The third band (often double), found in the region 3200 cm^{-1} with primary aromatic amines, is quite sharp and does not vary in intensity with concentration as required for an intermolecular hydrogen bond (cf. Bellamy 1954). It is undoubtedly the first overtone of the intense NH_2 deformation frequency.

The curves in Figure 1 show that the frequencies for aniline remain sensibly constant at concentrations below 0·1M. We therefore believe that the frequencies, recorded for the various materials in Table 1, which were deter-

TABLE 1

N–H STRETCHING FREQUENCIES IN VERY DILUTE SOLUTION

Substituent in Aniline	Asymmetric N–H Stretching Frequency (cm^{-1})	$10^{-3}\ \varepsilon_{max.}$ ($cm^2\ mol^{-1}$)	Symmetric N–H Stretching Frequency (cm^{-1})	$10^{-3}\ \varepsilon_{max.}$ ($cm^2\ mol^{-1}$)	Solvent	Concentration (mol l^{-1})
——	3482	30	3395	35	C_2Cl_4	$2{\cdot}70\times10^{-3}$
4-Nitro-	3506	80	3414	205	C_2Cl_4	$2{\cdot}18\times10^{-3}$
	3508	75	3413	230	$CHCl_3$	$7{\cdot}19\times10^{-3}$
3-Nitro-	3493	90	3405	160	C_2Cl_4	$1{\cdot}45\times10^{-3}$
	3496	55	3406	105	$CHCl_3$	$6{\cdot}59\times10^{-3}$
2-Nitro-	3519	195	3398	250	C_2Cl_4	$1{\cdot}25\times10^{-3}$
	3509	145	3393	205	PhCl	$1{\cdot}19\times10^{-1}$
	3505	160	3390	235	Benzene	$1{\cdot}45\times10^{-1}$
	3522 3504 sh.	160	3399	230	$CHCl_3$	$5{\cdot}25\times10^{-3}$
	3496	175	3386	235	$PhNO_2$	$1{\cdot}12\times10^{-1}$
	3484	140	3361	205	Acetone	$6{\cdot}55\times10^{-1}$
	3466		3346		Dioxan*	
2 - Nitro - 3 - methoxy- ..	3507	120	3402	175	C_2Cl_4	$2{\cdot}23\times10^{-3}$
2-Nitro-3-methyl-	3505	130	3402	210	C_2Cl_4	$5{\cdot}08\times10^{-3}$
	3499	100	3396	155	PhCl	$1{\cdot}41\times10^{-1}$
	3485	105	3369	185	Acetone	$6{\cdot}20\times10^{-1}$
2-Nitro-3-chloro-	3505	135	3403	215	C_2Cl_4	$1{\cdot}48\times10^{-3}$
2,3-Dinitro- ..	3516		3402		C_2Cl_4	Very dilute
	3517 3508 sh.	145	3403	250	$CHCl_3$	$4{\cdot}21\times10^{-3}$
2 - Nitro - 4 - methoxy- ..	3513	95	3396	120	C_2Cl_4	$3{\cdot}08\times10^{-3}$
2,4-Dinitro- ..	3518		3392		C_2Cl_4	Very dilute
	3463		3324		Dioxan*	
2 - Nitro - 6 - methoxy- ..	3523	185	3399	185	C_2Cl_4	$2{\cdot}02\times10^{-3}$
2-Nitro-6-methyl-	3520	160	3392	185	C_2Cl_4	$2{\cdot}41\times10^{-3}$
	3520		3394		CCl_4	c. $1{\cdot}5\times10^{-3}$
2-Nitro-6-chloro-	3508	230	3392	230	C_2Cl_4	$1{\cdot}22\times10^{-3}$
	3511		3394		CCl_4	c. 1×10^{-1}
	3510	205	3391	235	$CHCl_3$	$1{\cdot}80\times10^{-3}$
2,6-Dinitro- ..	3476	405	3361	285	C_2Cl_4	$2{\cdot}45\times10^{-3}$
	3477	470	3364	320	$CHCl_3$	$4{\cdot}11\times10^{-3}$
2,4,6-Trinitro- ..	3457	275	3344	235	C_2Cl_4	$1{\cdot}41\times10^{-3}$
	3444		3312		Dioxan*	
2 - Nitro - 5, 6 - benzo-† ..	3520	385	3364	465	C_2Cl_4	$4{\cdot}79\times10^{-3}$
2 - Nitro - 3, 4 - benzo‡ ..	3508	160	3385	165	C_2Cl_4	$1{\cdot}12\times10^{-3}$
N-Acetyl-4-nitro-	3429				$CHCl_3$	c. $1{\cdot}17\times10^{-3}$
N-Acetyl-2-nitro-	3364	155			C_2Cl_4	$1{\cdot}44\times10^{-1}$
	3368	120			$CHCl_3$	$1{\cdot}67\times10^{-3}$

* Hambly and Bonnyman (1958).

† 2-Nitro-1-naphthylamine.

‡ 1-Nitro-2-naphthylamine.

mined at concentrations below 0·10M in carbon tetrachloride or tetrachloroethylene, are strictly comparable.

The effect of hydrogen bonding between a primary amino and an *ortho*-nitro group would be to weaken one of the N–H bonds, so that the interaction between the symmetric (ν_s) and asymmetric (ν_{as}) motions would be reduced. This would result in the higher (ν_{as}) frequency moving towards the mean value ($\sim$3450 cm^{-1}) while the lower (ν_s) frequency would show a much larger shift to lower frequencies. The change would be similar to that which is fully developed when one hydrogen atom is replaced by deuterium (Table 2). When both hydrogen atoms are involved in the symmetrical formation of hydrogen bonds both frequencies will be depressed by similar amounts.

TABLE 2

EFFECT OF DEUTERATION ON N–H STRETCHING FREQUENCIES

Compound	Asymmetric Stretching Frequency, ν_{as} (cm^{-1})			Symmetric Stretching Frequency, ν_s (cm^{-1})			Reference
	NH_2	NHD	ND_2	NH_2	NHD	ND_2	
Aniline ..	3478	3430	2572	3395	2545	2493	Califano and Moccia (1957)
4-Nitroaniline	3508	3458	2626	3413	2560	2471	Califano and Moccia (1957)
2-Nitroaniline	3519	3480 3448	2637 2632	3398	2565 2550	2491 2474	Present work

Our results, combined with those of Califano and Moccia (1957) and Orville-Thomas, Parsons, and Ogden (1958), which are in good agreement when the same compounds have been measured, give a linear correlation between ν_{as} and ν_s for nine *meta*- and *para*-substituted anilines

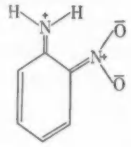
$$\nu_{as} = 1{\cdot}415\nu_s - 1325 \text{ cm}^{-1}. \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

This can also be expressed in terms of a linear relationship (Fig. 2) between the mean stretching frequency $\nu_m = \frac{1}{2}(\nu_{as} + \nu_s)$ and the separation $\delta = \nu_{as} - \nu_s$. This indicates that the inductive and mesomeric effects which are changing the bond strengths are responsible for the magnitude of the interaction be ween the two frequencies, which is probably due to the H–H repulsion. The values for solutions of methylamine (but not those for *n*-butylamine *iso*propylamine, and *tert.*-butylamine (Orville-Thomas, Parsons, and Ogden 1958)) fall close to this line. The values of ν_{as} indicate strengthening of the N–H bonds by substituents with net electron-attracting effects. This continues the effect already apparent in the passage from aliphatic to aromatic amines.

In the general case of inter- or intramolecular hydrogen bonding involving an energy reduction of the order of kT calories, two sets of vibration frequencies corresponding to the bonded and non-bonded forms, which will exist in equilibrium, are to be expected. These are found in solutions of alcohols in

non-polar solvents or in the classical example of weak intramolecular hydrogen bonding, *o*-chlorophenol (Pauling 1936). If the change in energy is much less than kT calories the material will be almost exclusively in the non-bonded form. Such duplication of frequencies is not found in crystals since one molecular form only is present in the lattice, nor is it found in any of our nitroamines where the observed N–H stretching bands are quite sharp.

If the very doubtful assumption is made that departures from equation (1) shown by *ortho*-substituted compounds are to be attributed entirely to hydrogen bonding, to the exclusion of other " *ortho* " effects, then ν_s for *o*-nitroaniline has been depressed by 26 cm^{-1} by this interaction. In 2,6-dinitroaniline and 2,4,6-trinitroaniline where the electron-attracting effects of the nitro groups would lead to an increase in both ν_{as} and ν_s, we find that both frequencies are lowered by 40 and 60 cm^{-1}, in the respective compounds, compared to those of 2-nitroaniline. The very weak hydrogen bonds of length 3·09 Å which occur in the crystal of *p*-nitroaniline produce changes in ν_s of 51 cm^{-1}. If the effects noted in 2,6-dinitroanilines are to be attributed to hydrogen bonding we must assume that the molecular configuration is determined by forces much more powerful than those involved in the hydrogen bonds and that it is not disturbed by molecular collisions. This would arise by the electronic distribution approximating to that of structure I:



(I)

(II)

This would involve the change of the hybridization about the amine nitrogen from sp^3 to sp^2 making it coplanar with the benzene ring and the nitro group (Francel 1952). With the groups held in this configuration the effect of hydrogen bonding could be observed as even a small additional term increasing the stability of the structure. The structure would involve increase in N–H bond strength, reduction in N–O bond strength, and increased repulsion between the hydrogen atoms due to decreased shielding by the bonding electrons. All these effects are reflected in the infra-red spectra found. Moreover, if the strongest hydrogen bonds are formed when the proton is collinear with the two electronegative atoms the weakness of the hydrogen bonds found here may depend in part on the fact that the N–H bond direction makes an angle of 32° with the N– – –O internuclear line (cf. Schroeder and Lippincott 1957).

Although our frequency values differ very considerably from those of Flett (1948) and Hathway and Flett (1949), we are in agreement with the latter workers, that the frequencies of N–H vibration in 2-nitro-1-naphthylamine show the effect of weak hydrogen bonding. The case of 1-nitro-2-naphthylamine is

more doubtful but Figure 2 shows that the vibrations of this compound have moved from the values common to the other 3-substituted-2-nitroanilines towards those of hydrogen bonded compounds. The comparison of 2-nitroacetanilide with 4-nitroacetanilide confirms the presence of a hydrogen bond of moderate strength in the former compound (Chaplin and Hunter 1938 ; Buswell, Downing, and Rodebush 1939).

Orville-Thomas, Parsons, and Ogden (1958) consider that the ratio of intensities of ν_s to ν_{as} decreases in the passage from aliphatic to aromatic primary amines because of the reduced importance of the lone pair electrons originally associated with the amine nitrogen atom. Our results do not conform to this generalization for the ratio is higher in *p*- and *o*-nitroanilines than in aniline itself. The intensity ratio is higher in *m*-nitroaniline than in the *ortho*-compound and increases with 3-substitution but decreases with 6-substitution in 2-nitroanilines. The ratio is especially lowered in the 2,6-dinitroanilines.

(*b*) *Solvent Effects*

The N–H stretching frequencies found for solutions in carbon tetrachloride, tetrachloroethylene, and chloroform agree within experimental error except for the development of a shoulder at ~3505 cm^{-1} in chloroform solutions of 2-nitro- and 2,3-dinitroaniline. There is evidence for a weak interaction with aromatic molecules in that both ν_s and ν_{as} decrease when benzene or chlorobenzene is used as a solvent. These changes are specific and cannot be allotted to simple polarizability effects as reflected in the refractive indices of the solvents (Bayliss, Cole, and Little 1955). It is therefore not correct, in the case of nitroamines, to allot the difference between the stretching frequencies in dilute carbon tetrachloride solution and in the solid state to the effect of hydrogen bonding alone (cf. Pimentel and Sederholm 1956). The small further decrease that occurs when nitrobenzene is the solvent indicates that intermolecular hydrogen bonding must be extremely weak. Acetone and particularly dioxan show much stronger interaction with the amine group.

(*c*) *Deformation Frequency of* NH_2 *Group*

The " scissor " deformation frequency of the aromatic primary amines has a remarkable constancy, independent of the state of aggregation and the concentration of solutions. In all the compounds studied its intensity was much higher than that of the aromatic frequencies which occur above 1600 cm^{-1} in nitro-substituted compounds. The highest frequency and the highest intensity were found in 2,6-dinitroaniline as was expected in view of the other evidence for hydrogen bonding in this compound.

It has been suggested (Colthup 1950 ; Bellamy 1954) that a strong absorption in the region 1250–1340 cm^{-1} is found with all aromatic amines and is related to the vibration of the C–N bond which has " partial double bond " character. We find either one or two bands in the appropriate region but the intensity of these is very variable (Table 3). The band in *p*-nitroaniline is stronger and at higher frequencies than in the *o*-nitroanilines, but was not observed in *p*-nitro-*NN*-dimethylaniline.

(*d*) *Absorption Bands of NO_2 Groups*

We have recorded the spectra of some mono- and dinitro aromatic hydrocarbons, in addition to those of the nitroanilines, in order to have suitable references for the variation of the symmetric and asymmetric stretching frequencies of the nitro group when free and when sterically hindered. There has been considerable discussion of the variation of these frequencies due to steric effects. van Veen, Verkade, and Wepster (1957) found a variation of only 9 cm^{-1} for the asymmetric frequency (1528–1537 cm^{-1}) in 23 nitrohydrocarbons in *cyclo*hexane solution. In only two cases of 2,6-substitution was the value higher (1 cm^{-1}) than in nitrobenzene. The values found by Brown (1955) in chloroform solutions are slightly lower than those of van Veen, Verkade, and Wepster (1957) and show a more definite correlation with the electron-attracting and donating properties of substituent groups. In no case does ν_{as} come within 30 cm^{-1} of its value in nitromethane (1580 cm^{-1}). The symmetrical stretching frequency shows a much greater range, from 1349 cm^{-1} in nitrobenzene to 1380 cm^{-1} in nitrodurene, showing a simple correlation with the effect of steric hindrance by alkyl groups.

The interpretation of these effects, which is given by van Veen, Verkade, and Wepster (1957), is that the sterically hindered nitro-compounds have the nitro group rotated out of the plane of the aromatic ring thus reducing its conjugation and increasing the bond order of the N–O bonds. This argument appears to be based on a similar phenomenon observed with 2,6-disubstituted acetophenones (Bellamy 1954), and the X-ray study of picryl iodide (Huse and Powell 1940), which indicates that the 2- and 6-nitro groups are rotated to 80° from the plane of the ring by the iodine atom. The observed frequencies in the alkyl-substituted nitrobenzenes do not support such an explanation since the increase in bond order, with consequent reduction of the negative charge on the oxygen atoms, would on the simple " central force field " model cause a larger increase in ν_{as} than in ν_s. If the *ortho*-alkyl groups bend the nitro group to one side of the plane of the ring rather than rotate it from the plane, then conjugation and bond orders would not be greatly affected. Repulsion between the oxygen atoms and the alkyl groups would increase the symmetric frequency in which they come more closely in contact, while it would make little change in ν_{as} for which the increases in one repulsion would be balanced by a decrease in the other.

In the nitroamines, the electron-donating character of the amine group will tend to reduce the bond orders in the nitro group (structures I and II) so lowering both ν_{as} and ν_s as shown in Tables 3*A* and 3*B*. We find that 2,3-dinitroaniline, like 1,2-dinitrobenzene, shows a doubling of ν_s but, whereas the latter shows only one asymmetric frequency, the former shows a separation into a frequency similar to that of *o*-dinitrobenzene and another similar to that of *o*-nitroaniline. The behaviour of the asymmetric NO_2 frequency in *NN*-dimethyl-4-nitroaniline is unusually sensitive to the state of aggregation. Franck, Hörmann, and Scheibe (1957) and Kross and Fassel (1957) give ν_{as} as 1489 and 1522 cm^{-1} respectively for the solid compound. van Veen, Verkade, and Wepster (1957) give 1501 cm^{-1} for this frequency in *cyclo*hexane solution. We find that in

TABLE 3A

VIBRATION FREQUENCIES AND EXTINCTION COEFFICIENTS OF NITROHYDROCARBONS AND NITROANILINES 1650–1200 cm^{-1}

Nitrobenzene	2,6-Dimethylnitrobenzene	1,2-Dinitrobenzene	1,3-Dinitrobenzene	6-Methyl-2-nitroaniline	6-Methoxy-2-nitroaniline	6-Chloro-2-nitroaniline	2,6-Dinitroaniline	2-Nitroaniline		
$5\cdot36\times10^{-2}$M C_2Cl_4	$3\cdot66\times10^{-2}$M C_2Cl_4	$1\cdot61\times10^{-2}$M C_2Cl_4	$1\cdot13\times10^{-1}$M C_2Cl_4	$2\cdot41\times10^{-2}$M C_2Cl_4	$2\cdot02\times10^{-2}$M C_2Cl_4	$1\cdot22\times10^{-2}$M C_2Cl_4	$2\cdot45\times10^{-2}$M C_2Cl_4	$1\cdot25\times10^{-2}$M C_2Cl_4	$5\cdot25\times10^{-2}$M $CHCl_3$	Solid Film
							1635 (1640)			
1620 (45)				1622 (655)	1624 (440)	1618 (680)	1614 (75)	1624 (1050)	1625 (1000)	1627
1607 (80)	1612 (45)		1615 (200)							
		1600 (100)	1603 (200)					1583 (sh.)	1585 (200)	
	1585 (30)			1577 (155)	1584 (100)	1576		1575 (370)	1575 (375)	1573
						1564 (170)	1566 (440)			
		1549 (1860)	1544 (1260)			1540 (210)				
1532 (1460)	1531 (1080)		1516 (125)	1523 (1270)	1528 (1620)	1518 (1570)	1523 (1390)	1515 (1700)	1513 (1250)	1508
						1508 (sh.)	1512 (465)	1503 (230)	1502 (sh.)	1495
1480 (100)	1482 (sh.)							1480 (95)	1480 (75)	1476
	1469 (95)			1469 (200)	1466 (sh.145)					
	1446 (85)			1452 (375)	1455 (290)	1448 (270)	1450 (370)	1445 (435)	1442 (330)	
				1436 (125)						1429
	1383 (sh.)		1379 (60)	1381 (90)	1381 (165)					
	1370 (310)	1368 (330)	1369 (80)	1355 (340)	1352 (70)	1351 (345)	1358 (230)	1354 (sh. ?)	1361 (sh.)	1365
1348 (1150)		1348 (510)	1353 (sh.) / 1344 (1950)	1349 (sh.)			1337 (170),	1344 (980)	1345 (1080)	1349
1315 (55)				1325 (680)	1330 (730)	1318 (345)	1300 (430)			
				1278 (sh.180)	1278 (120)	1270 (465)	1276 (2010)	1288 (365)	1287 (320)	1282
			1269 (70)	1257 (610)	1263 (295)	1254 (170)		1261 (940)	1260 (950)	1250
					1219 (1140)					1242

TABLE 3B

VIBRATION FREQUENCIES AND EXTINCTION COEFFICIENTS OF NITROANILINES 1650–1200 cm^{-1}

3-Nitroaniline		4-Nitro-aniline	3-Chloro-2-nitro-aniline	2,3-Dinitro-aniline	3-Methyl-2-nitro-aniline	3-Methoxy-2-nitro-aniline	*NN*-Dimethyl-4-nitroaniline			*NN*-Di-methyl-3-nitro-aniline
$6\cdot59\times10^{-2}$M $CHCl_3$	Solid Film	$7\cdot19\times10^{-2}$M $CHCl_3$	$1\cdot48\times10^{-2}$M C_2Cl_4	$4\cdot21\times10^{-2}$M $CHCl_3$	$5\cdot08\times10^{-2}$M C_2Cl_4	$2\cdot23\times10^{-2}$M C_2Cl_4	$1\cdot15\times10^{-2}$M CCl_4	$3\cdot64\times10^{-1}$M $CHCl_3$	Solid in KCl	Solid Film
	1643 (sh.)									1635 (sh.)
1631 (455)	1624	1624 (990)	1615 (610)	1629 (890)		1625 (650)				
	1608	1600 (870)	1601 (380)		1611 (740)	1613 (510)	1606 (sh.)	1606 (sh.)	1606	1617
									1601	
1585 (90)	1588			1594 (170)			1596 (1330)	1596 (1060)	1592	
1571 (75)	1567		1568 (305)	1572 (590)	1584 (235)	1583 (520)			1582	1567
				1547 (1050)						
1530 (1530)	1525		1526 (940)	1523 (920)	1516 (1070)	1523 (1070)	1519	1523 (250)	1530	1528
		1505 (740)					1504			
1486 (95)	1488	1493 (80)						1492 (435)		
	1481	1475 (80)	1466 (270)		1472 (235)	1471 (230)		1488 (390)	1486	
	1448	1443 (80)		1452 (160)	1454 (155)		1445	1446 (100)		1446
										1440
	1403				1383 (90)					1415
	1376			1366 (175)						1378
1354 (1100)	1357		1349 (380)	1351 (550)	1352 (415)	1360 (540)				1357
1335 (210)		1336 (1530)			1344 (sh.)					
1321 (155)					1339 (sh.)	1333 (240)	1329 (2220)	1318 (1980)		1331
1309 (115)		1310 (1050)								
1271 (120)			1281 (290)	1283 (330)	1277 (270)	1275 (520)				

the solid (KCl disk) there are bands at both 1530 and 1486 cm^{-1} and in chloroform solution at 1524 and 1491 cm^{-1}. In carbon tetrachloride there is an incompletely resolved, double band 1519, 1504 cm^{-1}, with the intensity greater at the lower frequency. It would appear that there are two vibrations interacting with

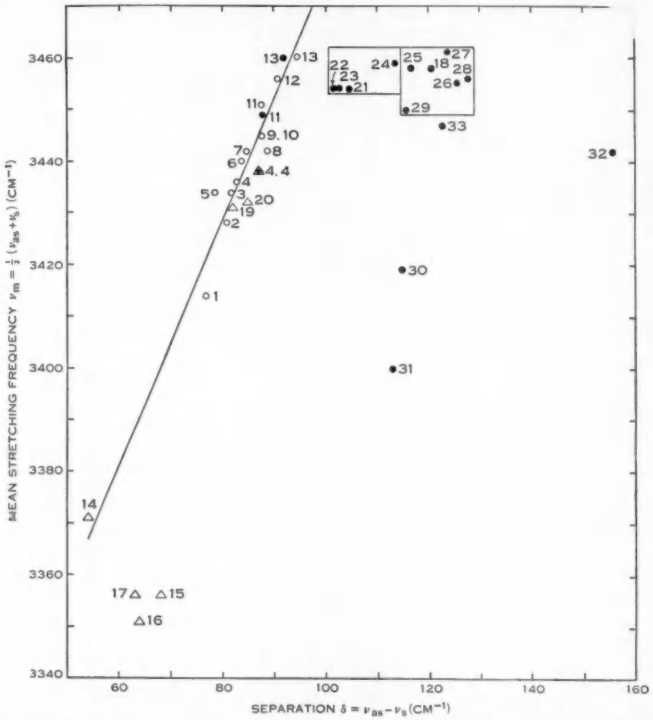


Fig. 2.—Relation between $\nu_m = \frac{1}{2}(\nu_{as}+\nu_s)$ and $=\nu_{as}-\nu_s$ for N–H stretching frequencies of aromatic amines.

1, *p*-Phenylenediamine; 2, *p*-toluidine; 3, *m*-phenylenediamine; 4, aniline; 5, *p*-fluoroaniline; 6, *p*-chloroaniline; 7, *p*-bromoaniline; 8, *p*-iodoaniline; 9, *m*-chloroaniline; 10, *m*-bromoaniline; 11, *m*-nitroaniline; 12, *p*-acetoaniline; 13, *p*-nitroaniline; 14, methylamine; 15, 1-propylamine; 16, 2-propylamine; 17, 1-butylamine; 18, 2-nitroaniline; 19, 1-naphthylamine; 20, 2-naphthylamine; 21, 2-nitro-3-methoxyaniline; 22, 2-nitro-3-methylaniline; 23, 2-nitro-3-chloroaniline; 24, 2,3-dinitroaniline; 25, 2-nitro-4-methoxyaniline; 26, 2,4-dinitroaniline; 27, 2-nitro-6-methoxyaniline; 28, 2-nitro-6-methylaniline; 29, 2-nitro-6-chloroaniline; 30, 2,6-dinitroaniline; 31, 2,4,6-trinitroaniline; 32, 2-nitro-1-naphthylamine; 33, 1-nitro-2-naphthylamine.

○ Califano and Moccia (1957); △ Orville-Thomas, Parsons, and Ogden (1958); ● Present work.

one another, presumably the aromatic frequency (19b. in the notation of Pitzer and Scott 1943), which is at 1485 cm^{-1} in benzene, and ν_{as} for the nitro group. Under these conditions it is not satisfactory to select (cf. Franck, Hörmann, and Scheibe 1957; van Veen, Verkade, and Wepster 1957) the strongest band

in this region as ν_{as} for the nitro group. In both *p*-nitroaniline and *NN*-dimethyl-4-nitroaniline the usual relationship of intensities is reversed and ν_s is stronger than ν_{as}. In 3-substituted-2-nitroanilines the value of $\nu_{as}-\nu_s$ for the N–H stretching frequencies is smaller than in *o*-nitroaniline and its 6-substituted derivatives (Fig. 2). This is to be coupled with the higher values of ν_s for the nitro group in the 3-substituted anilines as indicating that there is a steric effect acting on the nitro group and that this has reduced somewhat the conjugation between nitro and amino groups.

(*c*) *Evidence for Intramolecular Hydrogen Bonding in* o-*Nitroamines*

(i) *Volatility and Solubility in Non-Polar Solvents.*—Like *o*-nitrophenol and *o*-hydroxybenzaldehyde, *o*-nitroaniline may be separated from the corresponding *para*-compound by steam distillation. It has been established that the first two compounds contain intramolecular hydrogen bonds, and by analogy such bonding has been inferred for *o*-nitroaniline. However, the boiling points and melting points of the three simple nitroanilines form a regular sequence and the molar heats and entropies of evaporation of the *ortho*- and *meta*-compounds at their boiling points show very small differences (Table 4). Because of the

TABLE 4

PHYSICAL PROPERTIES OF NITROANILINES

Compound	Boiling Point (°C)	Melting Point (°C)	$\Delta H_{evap.}$* (kcal mole^{-1})	$\Delta S_{evap.}$* (cal mole^{-1} deg^{-1})
2-Nitroaniline ..	284·1	72·0	15·27	27·4
3-Nitroaniline ..	306·4	114·0	15·75	27·2
4-Nitroaniline ..	331·7	147·0	18·49	30·6

* Calculated from vapour pressure data (Jordan 1954).

differences in the lengths of the dipoles, the dipole moment of 2-nitroaniline (4·26 D) is much smaller than that of 4-nitroaniline (6·17 D) (Vassiliev and Syrkin 1941). This could well account for the lowered lattice energy which makes the *ortho*-compound more soluble in non-polar solvents and for the difference in latent heat of evaporation. In 3-nitroaniline the smaller transfer of charge between the amine and nitro group partly compensates for the difference in length of the dipoles so that the intermolecular forces are closer to those in the *ortho*- than to those in the *para*-compound.

(ii) *Polarographic Reduction Potentials.*—Holleck and Marsen (1953) and Holleck, Marsen, and Exner (1954) claim to distinguish intramolecular hydrogen bonding by a comparison of the half-wave potentials ($E_{\frac{1}{2}}$) for the reduction of *ortho*-, *meta*-, and *para*-substituted nitro- and aldehydic compounds. The extrapolated $E_{\frac{1}{2}}$ values, corresponding to pH 0, for *para*-substitution, are plotted on a line of arbitrary slope to provide an ordinate scale with $E_{\frac{1}{2}}$ as abscissa. The $E_{\frac{1}{2}}$ values for *meta*-substituted compounds are constant and lie along a vertical line when plotted with the same ordinate as the *para*-compound, while $E_{\frac{1}{2}}$ for *ortho*-substituted compounds lies on a sloping line in all cases except

those where intramolecular hydrogen bonding occurs. *o*-Nitroaniline is found to diverge in the same way as other *ortho*-compounds in which intramolecular hydrogen bonds are known to be present. Certain criticisms can be made of this work. The effects of *para*-substituents are very different in their order for the aldehyde and the nitro series, in particular the most positive values for $E_{\frac{1}{2}}$ for the former series occur with a *p*-formyl group and in the latter series with a *p*-nitro group, suggesting that a statistical effect is involved. In the former series the *p*-formyl compounds (for which the results plotted do not agree with the accompanying table) dominate the slope of the *ortho*-substituent line. A formyl substituent shows no such special influence in the reduction of nitro compounds.

The extrapolated values for the same compounds show large deviations from those of Astle and McConnell (1943), for example, Holleck, Marsen, and Exner's (1954) curve shows $-0{\cdot}055$ and $-0{\cdot}165$ V as the values of $E_{\frac{1}{2}}$ for *o*- and *p*-nitrophenols at pH 0, while the corresponding values found from the data of Astle and McConnell are $-0{\cdot}127$ and $-0{\cdot}367$ V.

The pK_a values for *o*- and *p*-nitroanilines are $-0{\cdot}17$ and $1{\cdot}11$ respectively (Hammett and Paul 1934), which would mean that even at pH 0 a considerable proportion of the *ortho*-nitro compound would be present as free base while the *p*-nitroaniline would be in the cationic form. This difference would be more pronounced at the experimental pH values. An aqueous medium with its high capacity for forming intermolecular hydrogen bonds is not a satisfactory medium for demonstrating the presence of weak intramolecular bonds. If the effects recorded by Holleck, Marsen, and Exner (1954) are due to hydrogen bonding then these bonds must be strong.

(iii) *Differential Adsorption of Isomers.*—Hoyer (1951) claimed to detect hydrogen bonding by the difference in adsorption of isomeric compounds from benzene solution on to a silica gel or alumina column. Thus 1-methylaminoanthraquinone, 1-aminoanthraquinone, and 1-amino-2-nitroanthraquinone passed rapidly down the column, while 2-methylamino, 2-amino-, and 1-amino-5-nitroanthraquinone were adsorbed. Presumably the 5-nitro group is supposed to conjugate with the carbonyl group, so lowering the tendency for formation of a hydrogen bond between amine and carbonyl. However, in the case of nitronaphthylamines Hoyer (1953) found that 1-amino-5-nitronaphthalene in which no hydrogen bonding is possible and 1-amino-8-nitronaphthalene were the least adsorbed, while 1,2- and 2,1-nitronaphthylamines were strongly adsorbed on alumina. It is perhaps significant that the order found by Hoyer for the adsorption of the nitronaphthylamines is that of the pK_a of the conjugate acids (Bryson 1949).

(iv) *Ultraviolet Spectra.*—Hörmann and Endres (1955) found that 2,4-dinitroaniline does not absorb in the region of 350 mμ when dissolved in acetic acid or ethyl acetate. Strong absorption occurs in this region for the corresponding solutions of *N*-methyl-2,4-dinitroaniline and *NN*-dimethyl-2,4-dinitroaniline. They arbitrarily attribute this difference to the formation of an intramolecular hydrogen bond in 2,4-dinitroaniline. In *cyclo*hexane solutions of 2-nitroaniline and seven 3- or 6-substituted-2-nitroanilines, Dyall and Pausacker (1958) observed

absorption in the range 356–393 mμ with log $\varepsilon_{max.}$=3·37–3·76, while in 2,6-dinitroaniline where the infra-red spectrum leads us to infer weak intramolecular hydrogen bonding this band is displaced to 408 mμ with log $\varepsilon_{max.}$=3·99. The results in Table 1 indicate that primary amine groups in 2-nitroaniline and 2,4-dinitroaniline interact with acetone and dioxan as solvents more strongly than with the nitro groups in the same molecule or in nitrobenzene as solvent. It seems certain that they would also interact with acetic acid as solvent. We therefore cannot accept the interpretation of the spectra of 2,4-dinitroaniline and its derivatives, which is given by Hörmann and Endres. On the contrary we note that Smith and Walshaw (1957) found that, in a study of dipole moments of 2,4- and 3,5-disubstituted anilines in benzene and dioxan solutions, 2,4-dinitroaniline falls into line with compounds in which hydrogen bonding is not expected "in spite of the fact that some hydrogen bonding between the amino group and the *ortho*-nitro group must occur".

We conclude that hydrogen bonding of appreciable strength only occurs in nitroanilines where nitro groups are in both positions 2 and 6 with respect to the amino group.

IV. Acknowledgments

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HYDROGEN BONDING IN ORGANIC COMPOUNDS

II. AMINE-CARBONYL INTERACTIONS

By A. N. Hambly* and J. Bonnyman*

[*Manuscript received July 7, 1958*]

Summary

A comparison of the infra-red spectra of typical aromatic compounds, with a primary amine group adjacent to a carbonyl group, with the spectra of related compounds, shows that, in the former, weak hydrogen bonding occurs between the two groups. The strength of the bonds formed is in the order: 1-aminoanthraquinone > 2-aminoacetophenone > methyl anthranilate, and the changes in carbonyl frequency are comparable with those of the symmetric NH_2 stretching frequency. Stronger hydrogen bonds are formed in corresponding *ortho*-acetamido compounds.

A brief study of the NH_2 stretching frequencies of *o*-nitroamines in dioxan solution shows that there is considerable interaction between solute and solvent but this cannot be definitely attributed to intermolecular hydrogen bonding.

I. Introduction

The absence of hydrogen bonding between a primary amine group and a single *ortho*-nitro group that was deduced from the infra-red spectra recorded in Part I of this series (Dyall and Hambly 1958) suggested that some other cases of reported hydrogen bonding involving the primary amine group might also be in error or exaggerated in importance. In particular, there are examples involving amine and carbonyl groups where the hydrogen bonding is said to have only a slight influence on the N—H stretching frequencies but to have a much larger effect on the carbonyl frequency (Bellamy 1954, p. 216). In other cases the materials, which are very sparingly soluble in non-polar solvents, have been studied in the solid state thus introducing possible confusion with intermolecular hydrogen bonding.

II. Experimental

(*a*) *Apparatus*

The spectra were recorded with a Perkin-Elmer model 112, single-beam, double-pass, spectrometer using a calcium fluoride prism for the NH_2 stretching frequencies and either a calcium fluoride or sodium chloride prism for frequencies below 1700 cm^{-1}. Frequencies of isolated absorptions are estimated to be correct to ± 2 cm^{-1}.

(*b*) *Materials*

The amines used were commercial samples, purified by recrystallization or distillation. The acetyl derivatives were prepared by treatment of the amines with acetic anhydride in the standard manner and were purified by recrystallization from ethanol or light petroleum.

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III. Results and Discussion

(*a*) *Amino Ketones*

The infra-red absorption frequencies of 4-aminoacetophenone, 4-aminopropiophenone, and 2-aminoacetophenone, as determined in dilute solutions in carbon tetrachloride, are presented in Table 1.

These show that, in the *ortho*-compound, the value of ν_{as} is practically the same as in the *para*-compounds but that ν_s has been depressed by 65 cm^{-1}. We conclude that a weak intramolecular hydrogen bond has been formed and that, as in the case of 2,6-dinitroanilines, the relative positions of the groups forming the hydrogen bond is maintained, not by the bond itself, but by conjugation of the groups with the aromatic ring and with each other (cf. Part I of this series). This conjugation between the groups results in a lowering of the bond order and absorption frequency of carbonyl in both the *ortho*- and *para*-compounds. In dilute carbon tetrachloride solutions, we find that acetophenone has its carbonyl absorption at 1690 cm^{-1} and this is reduced to 1675 and 1678 cm^{-1} in *p*-aminoacetophenone and *p*-aminopropiophenone respectively. In the *ortho*-compound there is a further lowering of the carbonyl frequency to 1649 cm^{-1}.

It is well known that the carbonyl stretching frequency is sensitive to direct, as distinct from conjugative, influences from adjacent polar groups. Thus there is a marked difference in the carbonyl frequencies for the axial and equatorial isomers of 1-bromo*cyclo*hexanone (Jones and Sandorfy 1956, pp. 445–6). It cannot therefore be said that the difference of 26 cm^{-1} between the carbonyl frequencies in *o*- and *p*-aminoacetophenone is solely due to hydrogen bonding, but the combination of the changes in the symmetric NH and the carbonyl frequencies provides good evidence for such a bond.

(*b*) *Aminoanthraquinones*

The spectra of crystalline 1-amino, 2-amino-, and 1-methylaminoanthraquinone (I, II, and III) have been studied by Flett (1948) and Shigorin and Dokunikhin (1955). Because of the effects of intermolecular forces on the N—H stretching frequencies, one cannot make a decision regarding the presence of intramolecular hydrogen bonds from the spectra of solids unless the bonds are extremely strong. Shigorin and Dokunikhin however suggest that the higher of the amine stretching frequencies in crystalline I is due to hydrogen in an intermolecular hydrogen bond and the lower to hydrogen in an intramolecular hydrogen bond. The compound I, but not the compound II, is sufficiently soluble in carbon tetrachloride for the spectrum to be studied in dilute solution. This shows (Table 2) the small depression of the asymmetric NH_2 frequency and the larger depression of the symmetric frequency, which are typical of unilateral hydrogen bonding in primary amines (cf. Part I loc. cit.). The displacement is small compared with that found by others for the OH band in the corresponding hydroxyanthraquinone.

Flett (1948) found that in 1-hydroxyanthraquinone, where there is evidence for a strong intramolecular hydrogen bond, two frequencies occurred in the carbonyl region. One of these (1673 cm^{-1}) was at practically the same value as that found in anthraquinone (1676 cm^{-1}), while the other (1636 cm^{-1})

TABLE 1

INFRA-RED ABSORPTION FREQUENCIES OF AMINO KETONES CARBON TETRACHLORIDE SOLUTIONS

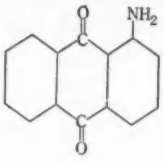
Absorption Frequency (cm^{-1})	*p*-Amino-acetophenone (cm^{-1})		*p*-Amino-propiophenone (cm^{-1})	*o*-Amino-acetophenone (cm^{-1})
From 3500–3400 ν_{as}	3499		3498	3500
ν_s	3408		3409	3343
From 1700–800 ..	Solid in Silver Chloride	Carbon Tetrachloride Solution	Carbon Tetrachloride Solution	Carbon Tetrachloride Solution
	1651	1675	1678	1649
	?	1619	1619	1617
	1593	1601	1601	1586
	1568	1577	1576	1555
	1519	1519	1518	1485
			1460	1452
	1442	1441	1437	
			1380	
	1364	1361	1357	1363
	1317, 1305	1312, 1300	1322 1302	1321
	1282	1279, 1276		1294
	1233		1232	1241
	1179	1177	1177	1163
	1134	1131	1131	
	1073	1074		
	1026		1013	1021
	972, 961, 942		952	955
	844, 837	831		
	825, 820			

TABLE 2

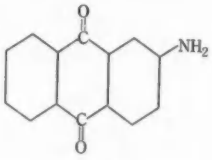
INFRA-RED SPECTRA OF AMINOANTHRAQUINONES

1-Aminoanthraquinone (cm^{-1})				2-Aminoanthraquinones (cm^{-1})			1-Methylamino-anthraquinone (cm^{-1})		
Carbon Tetra-chloride Solution	Paraffin Mulls			Paraffin Mulls			Paraffin Mulls		
Present Work	Present Work	Flett (1948)	Shigorin and Dokuni-khin (1955)	Present Work	Flett (1948)	Shigorin and Dokuni-khin (1955)	Present Work	Flett (1948)	Shigorin and Dokuni-khin (1955)
3502	3414	3420	3430	3429	3470	3455			
3331	3298	3300	3300	3327	3330	3340	3297	3300	3300
				3288 sh.	3220	3210			
				3199					
Absorptions 1680–1250 cm^{-1}									
1672	1665	1665		1673	1676		1671, 1664 sh.	1675	
1643	1638						1632	1635	
1603	1604	1612		1624	1625				
1593 sh.	1590			1611 sh.			1594		
	1580 sh.			1586			1588		
				1570					
1546	1543			1558			1563		
							1540		
1457	1453						1512		
							1506		
	1384						1499		
1373	1375								
1335	1324								
1315	1313								
1303									
1280	1284								

corresponds to the single absorption (1630 cm^{-1}) found by Hoyer (1957) for 1,4- and 1,5-dihydroxyanthraquinones where both carbonyl groups can participate in hydrogen bonding. Flett found only one carbonyl frequency (1673 cm^{-1}) for 2-hydroxyanthraquinone. However, in each of the spectra of compounds I, II, and III, he attributed two absorptions to carbonyl stretching and suggested that the separation was due to a lowering of the bond order of one carbonyl by mesomerism involving structures such as IV and V. Such mesomerism should be of comparable importance in 2-hydroxyanthraquinone but no separation of carbonyl frequencies was observed. He identified the strong bands at 1612 (we find 1603–4 cm^{-1}) and 1625 cm^{-1} in the spectra of I and II as the second carbonyl bands.



(I)



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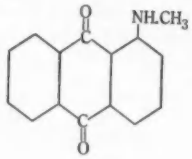

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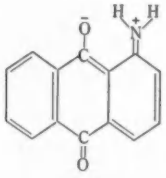

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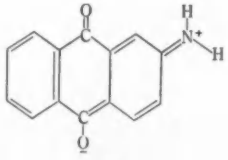


(V)

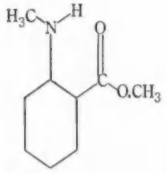
We find that, in the spectrum of I there are two bands 1665 and 1638 cm^{-1} for the solid and 1672 and 1643 cm^{-1} for dilute solution, of which the one of lower frequency is slightly more intense. These we attribute to the free and the hydrogen-bonded carbonyl groups, though other proximity effects may make a contribution to the frequency difference of 29 cm^{-1}. This is much less than the 53 cm^{-1} required by Flett's interpretation and conforms to the expectation that the depression of frequency will be smaller than that found for 1-hydroxyanthraquinone where a strong hydrogen bond is formed. It is also in good agreement with the order of separation of the carbonyl frequencies of *o*- and *p*-aminoacetophenones. The band at 1604 cm^{-1} is due to the NH_2 scissor deformation and is the band which disappears on methylation (Table 2). The carbonyl absorptions of I are also in close correspondence with those of III instead of showing a large difference in the lower frequency.

We also differ from Flett in the interpretation of the spectrum of II. The magnitude of the depression of the frequency of the carbonyl group, due to resonance involving structure V, would not be expected to exceed 15 cm^{-1}, the difference between the carbonyl frequency in acetophenone and that in its *para*-amino derivative where a similar resonance can occur. The lowering of the

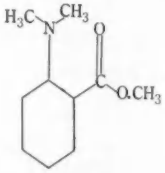
carbonyl bond order in anthraquinone compared with acetophenone would in fact make derivatives of the former less sensitive to conjugative effects. We cannot therefore accept the 1624 cm^{-1} absorption in the spectrum of II as a carbonyl frequency involving a displacement of 48 cm^{-1}. The 1624 cm^{-1} band is at the typical position for the NH_2 scissor vibration of a simple aromatic amine and we have found a strong band in this region in all the primary amines that we have studied. We conclude that compound II like 2-hydroxyanthraquinone shows only a single carbonyl absorption.

(*c*) *Amino-esters*

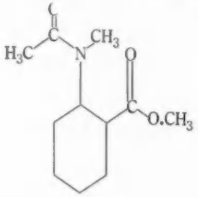
Rasmussen and Brattain (1949) deduced from a study of the infra-red spectra of methyl-*N*-methylanthranilate (VI); methyl-*NN*-dimethylanthranilate (VII); and methyl-*N*-methyl-*N*-acetyl-anthranilate (VIII); that there was hydrogen bonding between the amine and carbonyl groups in VI:



(VI)



(VII)



(VIII)

The hydrogen bonding was said to be more easily detected by the depression of the carbonyl frequency in VI to 1685 cm^{-1} compared to the values of 1727 and 1732 cm^{-1} in the compounds VII and VIII respectively, than by the value of the N—H stretching frequency, 3361 cm^{-1}. The depression of the carbonyl frequency was claimed to indicate a "chelation effect of almost the same magnitude as with salicylates".

We have measured the spectra of methyl anthranilate and ethyl *p*-amino-benzoate (Table 3). The small decrease in the symmetric NH_2 stretching frequency indicates a very weak chelation while the difference in the carbonyl frequencies is only 14 cm^{-1} compared to the 45 cm^{-1} difference observed by Rasmussen and Brattain (1949). The large difference found by these workers is due to a separate phenomenon. Conjugation between the amine and the carbonyl groups, and of each with the aromatic nucleus, is strongly developed only when the groups are coplanar with the ring. Steric interaction in VII and VIII will force the substituents out of the plane with a consequent rise in the bond order and stretching frequency of the carbonyl group. We attribute the greater part of the change in carbonyl frequency found by Rasmussen and Brattain to this effect and conclude that in VI, as in methyl anthranilate, hydrogen bonding if present is extremely weak.

It is significant that the lowering of the symmetrical NH_2 stretching frequency and of the carbonyl frequency increases in the order methyl anthranilate < 2-aminoacetophenone < 1-aminoanthraquinone. The values of the

carbonyl frequencies in the unsubstituted ethyl benzoate, acetophenone, and anthraquinone are 1722, 1690, and 1676 cm^{-1} respectively. This represents decreasing bond order in the carbonyl bond and therefore increasing negative charge on the oxygen atom of the group. The hydrogen bonds will be stronger as the charge on the oxygen atom increases.

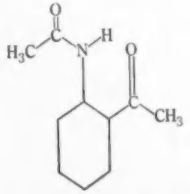
TABLE 3

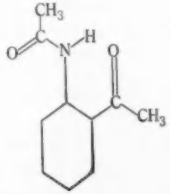
INFRA-RED ABSORPTION FREQUENCIES OF AMINO-ESTERS IN CARBON TETRACHLORIDE SOLUTION

Ethyl *p*-Amino-benzoate (cm^{-1})	Methyl Anthran-ilate (cm^{-1})	Ethyl *p*-Amino-benzoate (cm^{-1})	Methyl Anthran-ilate (cm^{-1})	Ethyl *p*-Amino-benzoate (cm^{-1})	Methyl Anthran-ilate (cm^{-1})
3499	3505	1711	1697	1392	
3406	3383	1621	1617	1369	
3375 (sh.)		1604		1333	1319
3216		1581	1590	1310	1296
3159		1532	1560	1278	1251
3043		1517		1173	1193
3018	3019	1479	1492	1120	1163
2982		1465		1109	1108
2958	2953	1445		1022	1029
2934		1437			
2967					
2875	2840				

(*d*) *Acetyl Derivatives*

The N—H stretching frequencies found in carbon tetrachloride solutions of *o*- and *p*-acetamidoacetophenone and 1-acetamidoanthraquinone are shown in Table 4. The large change in the N—H frequency for the two *ortho*-compounds shows that hydrogen bonding is stronger in the acetyl derivatives than in the parent amines, as was found also for 2-nitroacetanilide (cf. Part I of this series). The doubling of the frequency may be due to a *cis*- and *trans*-orientation of the *N*-acetyl group as in IX and X.





The planarity of such structures would be maintained by a partial double-bond character of the linkage between the acyl group and the nitrogen atom.

(*e*) *Intermolecular Bonding in Dioxan Solutions*

The differences between the dipole moments found for primary amines in 1,4-dioxan solutions and those found in benzene solution have been attributed

(Smith and Walshaw 1957) to the formation of hydrogen bonds from the amine to an oxygen atom of the ether. To test this hypothesis we have studied the NH_2 stretching frequencies of three nitroanilines in dioxan solution (Table 5).

Although it has been stated that dioxan is not sufficiently transparent in the region 3700–2600 cm^{-1} for use as a solvent in infra-red investigations with a cell thickness of 0·1 mm (Jones and Sandorfy 1956, p. 301), we find that the thoroughly purified and dry solvent (Hess and Frahm 1938) is quite suitable as a

TABLE 4

N–H FREQUENCIES OF ACETAMIDO-COMPOUNDS

1-Acetamido-anthraquinone (cm^{-1})	4-Acetamido-acetophenone (cm^{-1})	2-Acetamido-acetophenone (cm^{-1})
	3440	3294 sh.
3255		3257
3216		3229

solvent for the N—H and O—H stretching frequency region. The solvent and solutions must be protected from access of water vapour, absorption of which gives rise to two strong, broad bands at 3576 and 3510 cm^{-1}. These obscure the asymmetric N—H stretching frequency.

In this solvent the NH_2 stretching bands of nitroamines are considerably broadened and displaced to lower frequencies by interaction with the dioxan. The interaction is greater than is found with either nitrobenzene or acetone as

TABLE 5

N–H FREQUENCIES OF NITROANILINES

2-Nitroaniline			2,4-Dinitroaniline		2,4,6-Trinitroaniline	
Paraffin Mull (cm^{-1})	Carbon Tetrachloride Solution (cm^{-1})	Dioxan Solution (cm^{-1})	Carbon Tetrachloride Solution (cm^{-1})	Dioxan Solution (cm^{-1})	Carbon Tetrachloride Solution (cm^{-1})	Dioxan Solution (cm^{-1})
3480	3519	3366	3518	3463	3457	3444
3353	3398	3346	3392	3324	3344	3312
3217		3198				

solvent. It cannot be unambiguously established from these observations that hydrogen bonds are formed between the amine groups and dioxan. The frequencies in dioxan solution are successively lower for the mono-, di-, and trinitro compounds, which is the order of the acidities of the amine groups and therefore the order expected for the strengths of the hydrogen bonds to be formed. On the other hand both the symmetric and asymmetric frequencies

are depressed by comparable amounts, indicating that both hydrogen atoms are involved in the interaction. Severe steric requirements would be imposed in the formation of hydrogen bonds to two molecules of dioxan. In addition the value of the scissor deformation frequency, 1626 cm^{-1} for 2-nitroaniline in dioxan, is only 2 cm^{-1} greater than that found in carbon tetrachloride solution, whereas bilateral hydrogen bonding would be expected to raise this frequency considerably. The decrease in the stretching frequencies is of the same order as that found in the change from a dilute solution in a non-polar solvent to the crystalline state and may represent merely a general interaction between polar groups rather than the formation of strictly oriented hydrogen bonds. It has been noted in Part I of this series (Dyall and Hambly 1958) that the scissor deformation frequency is insensitive to such polar interactions.

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STUDIES OF THE OPTICALLY ACTIVE COMPOUNDS OF ANACARDIACEAE EXUDATES

IV. THE STRUCTURES OF THE REARRANGEMENT PRODUCTS FROM THE LONG CHAIN ALICYCLIC KETOALCOHOL OF TIGASO OIL IN ALKALI

By J. A. LAMBERTON*

[*Manuscript received June* 17, 1958]

Summary

The structure IIIa previously proposed for the β-diketone with an unsaturated side chain, obtained by the action of alkali on the optically active compound of Tigaso oil, is confirmed by the formation of methyl stearyl ketone and resorcinol monomethyl ether in the pyrolysis of the methyl ether (IV). An anomalous lithium aluminium hydride reduction of the methyl ether (IV) and other reactions are discussed. Unsuccessful attempts have been made to synthesize the tribasic acid resulting from sodium hypobromite oxidation of the β-diketone (IIIb).

I. INTRODUCTION

In Part II of this series (Dalton and Lamberton 1958*a*) it was suggested that the optically active compound I originally present in Tigaso oil undergoes cyclization in the presence of cold alcoholic alkali to the unsaturated *bicyclo*[3,3,1]nonane (IIa), and that on further treatment with hot alkali IIa is rapidly converted into a substance having the properties of a β-diketone with an unsaturated side chain. The unsaturated β-diketone was considered to consist predominantly or entirely of the compound IIIa, which on catalytic hydrogenation gives the corresponding saturated β-diketone (IIIb). The saturated β-diketone was also prepared by an alternative route in which IIa is reduced to the saturated *bicyclo*[3,3,1]nonane (IIb) and then heated briefly with alcoholic alkali.

By taking advantage of the solubility of the unsaturated β-diketone (IIIa) in aqueous sodium bicarbonate a convenient method has been found for its direct preparation from Tigaso oil without first isolating the compound I. The availability of the β-diketone (IIIa), and consequently of its dihydro derivative (IIIb), on a relatively large scale has allowed a fuller study of its reactions and confirmation of the structure already proposed. The direct preparation of the *bicyclo*[3,3,1]nonane (IIa) from Tigaso oil has been less successful because of the difficulty of separating IIa from the phenolic components of the oil without resorting to large-scale chromatography.

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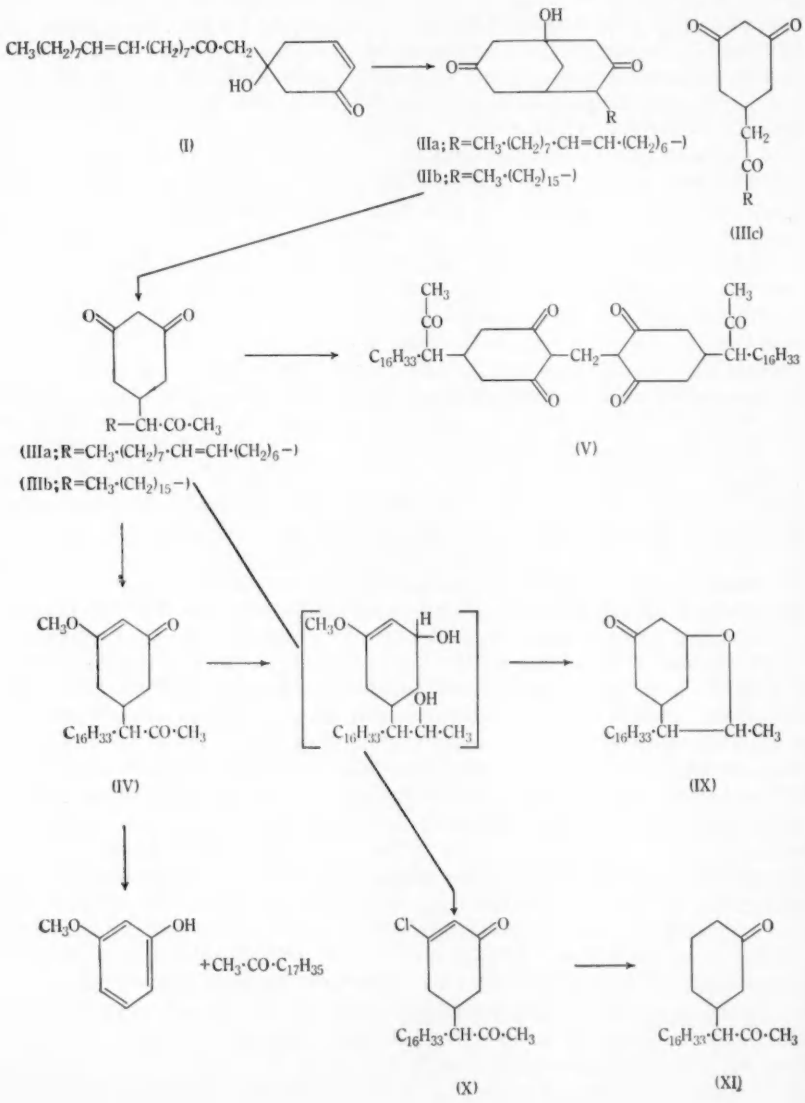
II. The Structure and Reactions of the β-Diketone (IIIb)

The structure of the saturated β-diketone (IIIb) has been established by a study of its methyl ether (IV) which is readily prepared by methylation with diazomethane. The infra-red absorption spectrum of IV has strong bands at 1645 and 1613 cm^{-1} similar to those shown by 3-ethoxy*cyclo*hex-2-enone, and in addition it has a strong carbonyl band at 1714 cm^{-1} due to the isolated carbonyl group. In ethanolic potassium hydroxide the methyl ether is rapidly reconverted into the β-diketone (IIIb).

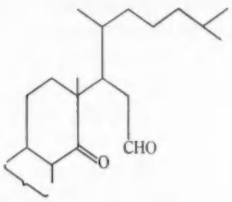
As previously reported, pyrolysis of the β-diketone (IIIb) yields methyl stearyl ketone but the other expected product of the reaction, resorcinol, is not formed in detectable quantity, and the methyl ether (IV) distils without decomposition at very low pressure. It has now been found, however, that when IV is heated at only moderately reduced pressure it breaks down almost quantitatively into methyl stearyl ketone and resorcinol monomethyl ether. This establishes the structure of the β-diketone as IIIb, for the only alternative structure (IIIc) which could lead to these pyrolysis products would not give the tribasic acid with sodium hypobromite. Condensation of the β-diketone IIIb with formaldehyde in the presence of piperidine yields the methylene *bis* derivative (V), which like IIIb itself readily undergoes pyrolysis into methyl stearyl ketone.

The same type of pyrolytic fission has been found to occur with the β-diketone (IIIb), its methyl ether (IV), the original compound (I), and the saturated hydroxydiketone derived from I by catalytic hydrogenation. These may be regarded as reverse Michael or, in the latter instance, as retroaldol reactions, and the closest analogy seems to be the reverse Michael fission used in certain steroid degradations. Thus Cornforth, Gore, and Popjak (1957) have described the fission of the ketoaldehyde (partial formula VI) by heating it in *cyclo*hexane at 210–220 °C, and a similar reaction involving the elimination of 2-methyl-*cyclo*hexanone has been used for the removal of ring A from compounds of the type VII. More usually reverse Michael reactions of this type have been base catalysed. Thus Turner (1950, 1954) found that a reverse Michael reaction takes place on heating the barium salt of Windaus acid, and Julia *et al.* (1953) achieved similar reactions under strongly alkaline conditions. To cause pyrolysis of the compound (partial formula VII) derived from the alkaloid conessine, Haworth and Michael (1957) found it necessary to heat a mixture of the compound and powdered potassium carbonate. With IIIb this modification results in a poorer yield of methyl stearyl ketone and no resorcinol. For fission to occur it is apparently necessary to have a carbon atom which is in a β-position to at least two carbonyl groups; but when 3-(nonadecan-2′-onyl)*cyclo*hexanone (VIII) (Dalton and Lamberton 1958*b*) is heated under the conditions used for the pyrolysis of the methyl ether (IV) no appreciable decomposition takes place.

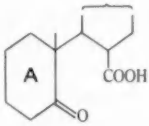
When enol ethers of *cyclo*hexane-1,3-diones are reduced with lithium aluminium hydride and the reaction products decomposed under acidic conditions, *cyclo*hex-2-enones are normally obtained. A number of examples of this reaction have been listed in the review by Micovic and Mihailovic (1955), and of these the simplest instance is the reduction of 3-methoxy*cyclo*hex-2-enone to *cyclo*hex-2-enone by Born, Pappo, and Szmuszkovicz (1953). The methyl


CH3(CH2)7CH=CH·(CH2)7·CO·CH2
HO
O
(I)
OH
O
O
R
(IIa; R=CH3·(CH2)7·CH=CH·(CH2)6–)
(IIb; R=CH3·(CH2)15–)
O
O
CH2
CO
R
(IIIc)
O
O
R—CH·CO·CH3
(IIIa; R=CH3·(CH2)7·CH=CH·(CH2)6–)
(IIIb; R=CH3·(CH2)15–)
CH3
CO
C16H33·CH
CH2
CH·C16H33
(V)
CH3O
O
C16H33·CH·CO·CH3
(IV)
CH3O
H
OH
OH
C16H33·CH·CH·CH3
O
O
C16H33·CH
CH·CH3
(IX)
CH3O
OH
+CH3·CO·C17H35
Cl
O
C16H33·CH·CO·CH3
(X)
O
C16H33·CH·CO·CH3
(XI)

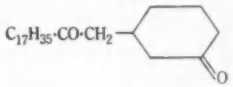
ether (IV) on reduction with lithium aluminium hydride by this method behaves in an anomalous way. The product is a crystalline compound, $C_{25}H_{46}O_2$, $[\alpha]_D$ $-4°$, which yields a mono-2,4-dinitrophenylhydrazone and a monoxime, but does not have the ultraviolet absorption of a conjugated carbonyl compound. The absence of an hydroxyl group, which was expected to result from the isolated carbonyl group, is shown by failure to form an acetate and by stability in chromic acid-pyridine solution. These results are confirmed by the infra-red absorption which shows only a strong carbonyl band at 1700 cm^{-1}. In the absence of both



(VI)



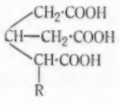
(VII)



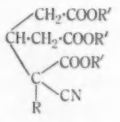
(VIII)

the conjugated carbonyl system and the hydroxyl group it seems probable that dehydration has occurred to give the compound IX containing a cyclic ether oxygen. In agreement with this formulation, IX is decomposed by heating in ethanolic potassium hydroxide solution, but the products of this reaction have not been fully examined.

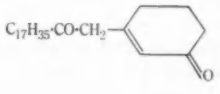
Previously it was found (Dalton and Lamberton 1958*a*) that reduction of the crude chloro compound (X) obtained by heating the β-diketone (IIIb) with phosphorus trichloride gives a low yield of a ketonic substance, $C_{25}H_{46}O_2$, which was not fully characterized. By using the modified conditions recently described by Ames and Davey (1957) for a similar type of reduction, this substance has now been obtained in better yield. It readily gives a monosemicarbazone and a mono-2,4-dinitrophenylhydrazone, and has a single carbonyl band at 1706 cm^{-1}, but it is shown to be the diketone (XI) by the formation of a dioxime and by the elimination of both oxygens on Wolff-Kishner reduction.



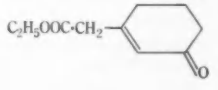
(XII)



(XIII)



(XIV)



(XV)

It was expected that the acid (XII; R=$C_{16}H_{33}$) obtained by sodium hypobromite oxidation of the β-diketone (IIIb) could be prepared by methods which have been reported in the literature for the synthesis of similar acids, but attempts to apply these methods were unsuccessful. It has been shown (Kohler and Reid 1925; Phillips, Acitelli, and Meinwald 1957) that a Michael condensation of methyl cyanoacetate with dimethyl glutaconate gives a high yield of trimethyl α-cyanomethanetriacetate (XIII; R=H) which on vigorous acid

hydrolysis gives methanetriacetic acid, and Gibbs and Henry (1939) obtained α-ethyl-β-carboxymethylglutaric acid (XII; R=C_2H_5) in 25 per cent. yield by hydrolysis of the condensation product from ethyl α-cyanobutyrate and diethyl glutaconate under similar conditions. Attempts to bring about this reaction using ethyl α-cyanostearate and diethyl glutaconate failed completely. A further synthesis was also attempted in which ethyl 3-chloroglutarate or ethyl 3-bromoglutarate was heated with the sodium derivative of ethyl α-cyanostearate, but no tribasic acid was isolated after hydrolysis of the resulting products. Although unsuccessful in this instance, the latter method does provide a somewhat more convenient preparation of triethyl α-cyanomethanetriacetate than does the original method of Kohler and Reid. Ethyl 3-chloroglutarate or 3-bromoglutarate, which are easily prepared by the action of the corresponding phosphorus pentahalide on ethyl 3-hydroxyglutarate, condenses very rapidly with the sodium derivative of ethyl cyanoacetate.

The unsaturated diketone (XIV) described in Part I of this series was shown to undergo decomposition in hot alkali to yield stearic acid and 3-methyl*cyclo*hex-2-enone. An analogous compound XV containing a vinylogous β-ketoester system has been described by Grewe, Nolte, and Rotzoll (1956). Like XIV, the compound XV gives a yellow solution in alkali, and is also decomposed by hot alkali to give 3-methyl*cyclo*hex-2-enone, the other products in this instance being carbon dioxide and ethanol. Although XIV is readily soluble in aqueous alkali it does not react with an ethereal solution of diazomethane.

III. Experimental

(*a*) *General*

As in Part I of this series (Dalton and Lamberton 1958*b*). The Tigaso oil used had $[\alpha]_D$ +6° (approximately).

(*b*) *Preparation of 1-Hydroxy-4-hexadecyl*bicyclo[*3,3,1*]*nonane-3,7-dione* (*IIb*) *from Tigaso Oil*

A solution of Tigaso oil (40 ml) in ethanol (500 ml) was cooled to 0 °C in an ice-bath and a cold solution of potassium hydroxide (10 g) in ethanol (100 ml) added. The mixture was kept at 0 °C for 30 min and then carefully diluted with cold water containing crushed ice. Ether extraction of the cold alkaline solution to separate the phenolic material proved troublesome and slow owing to emulsification. As an alternative, the cold solution was carefully acidified with dilute sulphuric acid and the whole oil, including the phenolic portion, extracted with ether and hydrogenated over platinum oxide in ethyl acetate solution. The hydrogenated *bicyclo*[3,3,1] nonane (IIb) was then isolated by chromatography on neutral alumina (see Part II). The yield of product melting at 104–105 °C was 3·7 g.

(*c*) *Preparation of* (*3'-Nonadecan-2'-onyl*)cyclo*hexane-3,5-dione* (*IIIb*) *from Tigaso Oil*

Tigaso oil (200 ml) was dissolved in ethanol (1000 ml) and a solution of potassium hydroxide (50 g) in ethanol (1500 ml) which had been heated almost to boiling point, was added. After mixing, the solution was heated on a steam-bath for 5 min and then cooled to room temperature in ice and water. After dilution with an equal volume of crushed ice and water, the solution was acidified with dilute sulphuric acid and the oil which separated was extracted with ether. The ether layer, after washing with water, was extracted with 5% aqueous sodium bicarbonate solution (3×500 ml) and the combined bicarbonate solutions washed several times with ether. During the extractions with sodium bicarbonate solution, emulsions were formed and it was

necessary to add ethanol to obtain separation. Acidification of the bicarbonate solution gave an oil which was extracted with ether; the solution was dried (Na_2SO_4) and the ether distilled.

The bicarbonate soluble portions from five such experiments were combined and hydrogenated in ethyl acetate over platinum oxide until rapid uptake of hydrogen ceased. It was necessary to use at least 200 ml of ethyl acetate for every 20 g of material to be reduced; otherwise the hydrogenation product crystallized. The combined yield from a total of 1000 g of Tigaso oil was 127 g of the crude β-diketone (IIIb) which melted at 103–105 °C after crystallization from ethyl acetate, and was readily purified by further crystallization.

(*d*) *Methyl Ether IV*

The crude β-diketone IIIb (15 g) obtained above was added to an excess of a cold ethereal solution of diazomethane. The crude product was purified by chromatography on neutral alumina when benzene elution and crystallization from light petroleum gave the pure methyl ether, m.p. 64–65 °C; $\lambda_{max.}$ 247, ε 14,190; $[\alpha]_D$ +1° (*c*, 2·1 in ethanol). There were infra-red bands ("Nujol mull") at 1714 cm^{-1} (strong), 1645 cm^{-1} (strong), and 1613 cm^{-1} (very strong). Heating a specimen of the methyl ether for 5 min in 2% alcoholic potassium hydroxide solution gave IIIb which melted at 106–108 °C after crystallization from ethyl acetate.

(i) *Pyrolysis of IV.*—The methyl ether IV (2 g) was gently heated in a small distilling flask at a pressure of 25–30 cm. The heating was adjusted so that the whole contents of the flask had distilled cleanly within 10 min and only a trace of dark residue remained. The distillate was dissolved in ether and the ether solution shaken with 1% aqueous sodium hydroxide solution.

Evaporation of the ether layer, after washing with water and drying over sodium sulphate, gave a crystalline residue which was chromatographed on alumina. Light petroleum eluted pure methyl stearyl ketone (1·2 g; m.p. 56–57 °C) which was identified as previously.

The sodium hydroxide solution was washed with ether, acidified, and extracted several times with ether. The combined ether extracts were dried (Na_2SO_4) and evaporated, and the oily residue distilled. The distillate (0·5 g) gave a weak ferric test in ethanolic solution, had a methoxyl content of 23·0%, and ultraviolet absorption maxima at λ 273, ε 2060 and λ 280, ε 1820. A specimen purified by further distillation was identified as resorcinol monomethyl ether by comparison of its infra-red spectrum with that of a synthetic specimen and by conversion into tribromoresorcinol monomethyl ether, which melted at 104 °C, alone and when mixed with a synthetic specimen (Found: C, 23·7; H, 1·6; OCH_3, 8·5%. Calc. for $C_7H_5O_2Br_3$: C, 23·2; H, 1·4; OCH_3, 8·6%).

(ii) *Lithium Aluminium Hydride Reduction of IV.*—The methyl ether IV (5·0 g) was dissolved in anhydrous ether and sufficient lithium aluminium hydride added for the reduction of two carbonyl groups. After heating at the boiling point of the mixture for 1 hr the crude product was isolated in the normal way and found to have no significant ultraviolet absorption. After heating in acetic acid-hydrochloric acid for 1 hr the product still showed no ultraviolet absorption. When it was chromatographed on alumina benzene eluted *compound IX* (2·1 g) which crystallized from ethanol in colourless needles, m.p. 74·5–75·5 °C; $[\alpha]_D$ −4° (*c*, 1·25 in chloroform). It had no significant ultraviolet absorption but a strong infra-red carbonyl band at 1700 cm^{-1} ("Nujol") (Found: C, 79·3; H, 11·9%; OCH_3, nil. Calc. for $C_{25}H_{44}O_2$: C, 79·4: H, 12·2%).

The *2,4-dinitrophenylhydrazone* from this ketone crystallized in yellow prisms, m.p. 138–139 °C, from ethanol (Found: N, 9·7%. Calc. for $C_{31}H_{50}O_5N_4$: N, 10·0%).

The *oxime* from ketone VI, m.p. 76–78 °C, crystallized in colourless prisms from ethanol (Found: N, 3·7%. Calc. for $C_{25}H_{47}O_2N$: N, 3·6%).

(*e*) *Methylene Bis-derivative V*

When a few drops of formaldehyde solution followed by a drop of piperidine were added to a hot ethanolic solution of IIIb, the solution rapidly became cloudy and an oil separated. The oil solidified and crystallized on cooling and was filtered and recrystallized several times from a large volume of ethanol. This gave colourless prisms, m.p. 42–43 °C, of the *methylene bis-derivative* (Found: C, 76·5; H, 11·1%. Calc. for $C_{51}H_{88}O_6$: C, 76·8; H, 11·1%).

(*f*) *3-(3′-Nonadecan-2′-onyl)cyclohexanone* (*XI*)

β-Diketone IIIb (2·5 g) was dissolved in dry chloroform (50 ml), phosphorus trichloride (1·5 ml) added, and the solution refluxed for 2 hr. The chloroform was then distilled and finally traces of chloroform and unreacted phosphorus trichloride were removed under reduced pressure. The use of less phosphorus trichloride or shorter periods of heating gave a product which, from its ultraviolet absorption, evidently contained unchanged β-diketone. When greater quantities of phosphorus trichloride were used or the reaction mixture was heated for longer periods, the solution became turbid and a sparingly soluble material separated. In the latter instance the crude chloroketone gave a cloudy solution in ethanol which was difficult to clarify, and the reduction did not proceed readily.

The residue was taken up in anhydrous ether and the solution passed through a short column of neutral alumina. Evaporation of the ether gave a colourless oil (1·3–1·5 g) which contained chlorine and had $\lambda_{max.}$ 235–236, ε 8450. The chloroketone (X) was reduced without further purification over palladous chloride (0·1 g) in absolute ethanol (50 ml) containing triethylamine (1 ml). When rapid uptake of hydrogen ceased (20–25 min) the solution was filtered and the ethanol partly distilled. After dilution with water and addition of hydrochloric acid, extraction with ether gave the crude diketone (XI), which was finally purified by chromatography on alumina. Benzene elution and crystallization from ethanol gave colourless prisms (0·5–0·6 g), m.p. 55–56 °C, $[\alpha]_D$ 0° or possibly very slight positive rotation. In " Nujol " there was a strong carbonyl band at 1706 cm^{-1} having a slight shoulder at 1693 cm^{-1} (Found : C, 79·1 ; H, 12·3%. Calc. for $C_{25}H_{46}O_2$: C, 79·4 ; H, 12·2%).

With semicarbazide acetate in ethanol, XI gave a semicarbazone, m.p. 157–158 °C, after crystallization from ethanol (Found : C, 71·7 ; H, 11·4 ; N, 9·5%. Calc. for $C_{26}H_{49}O_2N_3$: C, 71·7 ; H, 11·3 ; N, 9·7%). With hydroxylamine hydrochloride in pyridine at 100 °C for 20 min, XI gave a *dioxime* which melted at 50–51 °C, after crystallization from slightly aqueous ethanol (Found : N, 6·5%. Calc. for $C_{25}H_{49}O_2N_2$: N, 6·9%).

Wolff-Kishner reduction of the diketone XI gave a colourless oil which was purified by chromatography on alumina. After elution by light petroleum and distillation at 0·1 mm it showed no trace of carbonyl or hydroxyl absorption in the infra-red (liquid film) (Found : C, 86·1 ; H, 14·3%. Calc. for $C_{25}H_{50}$: C, 85·7 ; H, 14·3%).

(*g*) *Attempted Synthesis of the Acid* (*XII* ; $R=C_{16}H_{33}$)

(i) Ethyl α-cyanostearate, b.p. 205–210 °C at 2 mm, was prepared by the general method of Gagnon, Boivin, and Boivin (1950) (Found : C, 75·0 ; H, 11·6 ; N, 4·1%. Calc. for $C_{21}H_{39}O_2N$: C, 74·8 ; H, 11·6 ; N, 4·2%). Attempts to condense this compound with diethyl glutaconate under the conditions described by Kohler and Reid (1925), followed by hydrolysis of the crude reaction mixture by prolonged boiling in a mixture of glacial acetic acid and 70% aqueous sulphuric acid, gave only stearic acid. Heating the reaction product for a short period with acid led to the recovery of high yield of α-cyanostearic acid, m.p. 81–82 °C. The reaction also failed when piperidine or potassium *tert.*-butoxide in *tert.*-butanol were tried as the condensing agents.

(ii) Ethyl 3-bromoglutarate, b.p. 103–105 °C at 1 mm, was prepared by the action of phosphorus pentabromide on ethyl 3-hydroxyglutarate dissolved in carbon tetrachloride at 50–60 °C, according to the method described by Grundemann and Paul (1953) (Found : Br, 29·2%. Calc. for $C_9H_{15}O_4Br$: Br, 29·9%). In preparing ethyl 3-chloroglutarate from ethyl 3-hydroxyglutarate and phosphorus pentachloride the same method was followed, but it was necessary to work at a much lower temperature to reduce the formation of diethyl glutaconate. When phosphorus pentachloride was added to the solution of ethyl 3-hydroxyglutarate at 20–25 °C the product had $\lambda_{max.}$ 215, ε 2020, but addition at 0 °C and distillation gave substantially pure *ethyl 3-chloroglutarate*, b.p. 89–90 °C at 0·5 mm (Found : Cl, 15·9%. Calc. for $C_9H_{15}O_4Cl$: Cl, 16·7%). The ultraviolet absorption due to diethyl glutaconate impurity was only $\lambda_{max.}$ 215, ε 400.

Neither of these halogenated esters reacted in the desired manner with the sodium or potassium derivative of ethyl α-cyanostearate in ethanol or *tert.*-butanol. The reaction was also attempted by

preparing the sodium derivative of the cyanoester from sodium ethoxide in dry xylene, distilling part of the xylene to remove ethanol, and then adding ethyl 3-bromoglutarate. However, no tribasic acid was isolated after hydrolysis.

(iii) *Triethyl α-Cyanomethanetriacetate.*—Ethyl 3-chloroglutarate (22·5 g; 0·1 mol) was added to a solution of ethyl cyanoacetate (11·3 g; 0·1 mol) in absolute ethanol containing an equimolar proportion of sodium ethoxide. The mixture was heated at its boiling point for 30 min and worked up in the usual way. Triethyl α-cyanomethanetriacetate distilled as a faintly yellow oil, b.p. 159–162 °C at 0·5–1·0 mm, yield 85–90% (Found: C, 56·4; H, 7·1; N, 4·9%. Calc. for $C_{14}H_{21}O_6N$: C, 56·1; H, 7·0; N, 4·7%). Acid hydrolysis gave methanetriacetic acid agreeing in its properties with those reported by Kohler and Reid (1925) (Found: C, 44·2; H, 5·3%. Calc. for $C_7H_{10}O_6$: C, 44·2; H, 5·3%).

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METHYLSTEROIDS*

V. THE FACILITATION OF HYDROLYSIS OF STERICALLY HINDERED ACETOXY GROUPS BY CARBONYL GROUPS IN THE LANOSTEROL SERIES

By C. S. BARNES†

[*Manuscript received May* 29, 1958]

Summary

The facilitation of basic hydrolysis of sterically hindered acetoxy groups has been ex mined among the lanosterol oxo derivatives. It is found that an 11β-acetoxyl may be hydrolysed under mild conditions in the presence of a 7-oxo group or more easily when a 3,7-dioxo grouping is present. The 7α-acetoxy group is resistant to basic hydrolysis except in the presence of a 3- or 11-oxo group. Possible reasons for these effects are discussed.

I. HYDROLYSIS OF 11β-ACETATES

With saturated steroids of the *allo* series, it has long been recognized (e.g. Turner 1949) that while 11α-hydroxy or acetoxy groups behave normally to esterification or hydrolysis respectively, the 11β-position is too heavily hindered to allow reaction under the normal conditions. This inhibition is attributed largely to the crowding effect of the two axial-methyl substituents on C_{10} and C_{13} which bear a *cis*-1,3-relationship to the 11β-substituent (X, Fig. 1) which is also axial (for discussion, see Barton 1953). An 11β-hydroxyl may be acetylated only by using special conditions (Oliveto *et al.* 1953) and when formed the acetoxy compound is resistant to basic hydrolysis even with the most vigorous treatment. On the other hand, an 11α-substituent (Y, Fig. 1) is equatorially placed and so avoids the deactivating hindrances. An 11α-hydroxyl may be acetylated, and an 11α-acetoxyl may be hydrolysed without difficulty.

Similar arguments apply to lanosterol derivatives which are 4,4,14-trimethyl-*allo*steroids (Fig. 1). In Figure 2, these facts are demonstrated quantitatively by comparing the rate of hydrolysis of 3β,7β,11α-triacetoxylanostane (I) (Barnes and Palmer 1957), having an equatorial 11α-acetoxy group, with that of 3β,7β,11β-triacetoxylanostane (II; R=R′=Ac)‡ which has an axial 11β-acetoxy group, when refluxed with 0·3N ethanolic potassium hydroxide. It is seen that whereas the three acetoxyls of I are hydrolysed, with II (R=R′=Ac) which is epimeric at C_{11}, only the two less-hindered groups react. As confirmation of the resistance

* For Part IV of this series see Barnes (1957).

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‡ Prepared by the method of Barnes and Palmer (1957). In that paper the 11β-hydroxy compound II (R=Ac, R′=H) was obtained by several different methods, and its physical constants were revised. It is noted that Bentley *et al.* (1953) also obtained the 11β-hydroxy compound II (R=Ac, R′=H) by a method similar to one of those described, and found constants in excellent agreement with the revised figures.

of the 11β-acetoxyl to hydrolysis, the derived diol (II; R=H; R′=Ac) was also found not to be significantly attacked under the conditions used. For comparison the 3β-acetoxy group of III and the 3β,7β-diacetoxy groups (di-equatorial) of IV were easily hydrolysed.

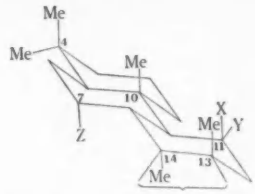


Fig. 1.—Spatial relationships of steroid substituents.

The influence of carbonyl groups on the rate of hydrolysis of the 11β-acetoxyl was studied with compounds V (R=Ac), VI (R=H, R′=Ac), and VII (R=H, R′=Ac) which were prepared by methods now to be described. Hydrolysis of the triacetate (II; R=R′=Ac) gave the monoacetoxydiol (II; R=H,

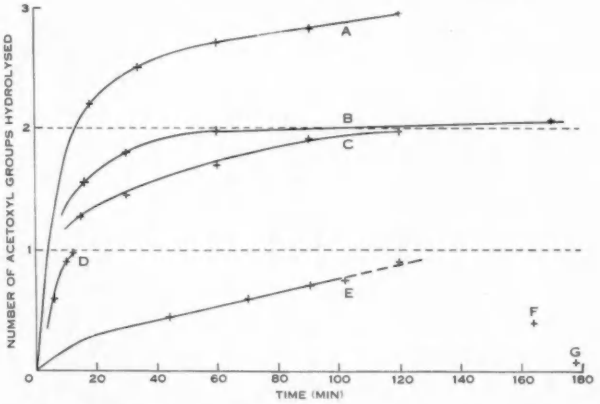
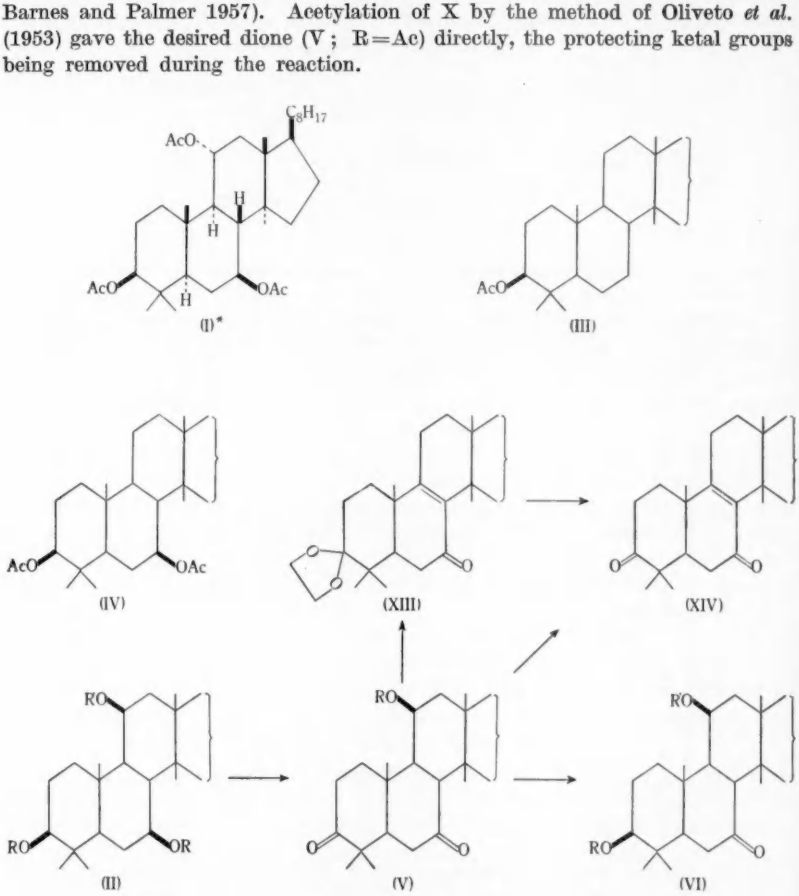


Fig. 2.—Hydrolysis of 11β-acetates with 0·3N ethanolic potassium hydroxide. *A*, 3β,7β,11α-Triacetoxylanostane (I); *B*, 3β,7β,11β-triacetoxylanostane (II; R=R′=Ac); *C*, 3β,7β-diacetoxylanostane (IV); *D*, 3β-acetoxylanostane (III); *E*, 11β-acetoxylanostane-3,7-dione (V; R=Ac); *F*, 11β-acetoxy-3β-hydroxylanostan-7-one (VI; R=H, R′=Ac); *G*, 11β-acetoxylanostane-3β,7β-diol (II; R=H, R′=Ac); 7β,11β-diacetoxylanostan-3-one (VII; R=H, R′=Ac).

R′=Ac), and 11β-acetoxylanostane-3,7-dione (V; R=Ac) was formed by chromic acid oxidation of this diol. The acetoxydiol was characterized by conversion to the dibenzoate (II; R=Bz, R′=Ac). The structure of the acetoxydione was confirmed by an independent synthesis from the trione VIII which gave the diketal IX on reaction with excess ethylene glycol. Lithium

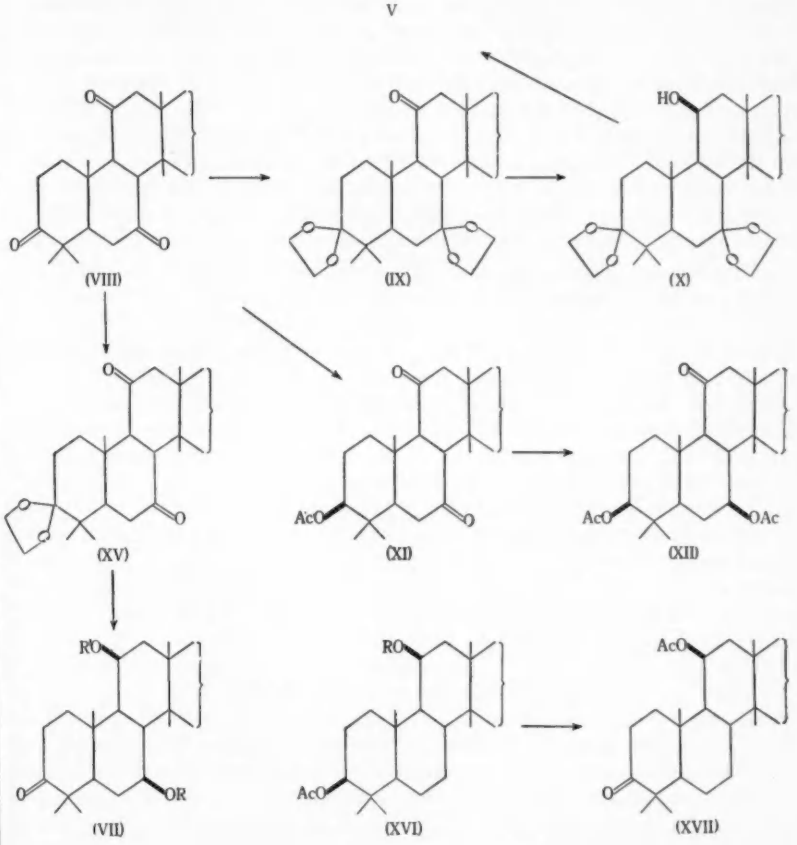
aluminium hydride reduction of IX gave the 11β-hydroxy compound X, the configuration of the reduced product being inferred from the known stereospecificity of the reduction at the 11-position (Sarett, Fewser, and Folkers 1951; Barnes and Palmer 1957). Acetylation of X by the method of Oliveto *et al.* (1953) gave the desired dione (V; R=Ac) directly, the protecting ketal groups being removed during the reaction.



* The stereochemistry of the carbon skeleton is identical in subsequent formulae.

The structure 3β,11β-diacetoxylanostan-7-one (VI; R=R′=Ac) had been tentatively assigned to a minor component isolated from the acetylated product of the reduction of the 7,11-dione (XI) (Barnes and Palmer 1957). Confirmation was obtained by an independent synthesis from V (R=Ac), which took advantage of the relative degrees of reactivity of the 3- and 7-oxo groups. Reduction with 1 mole-equivalent of sodium borohydride gave the 3β-hydroxy compound (VI; R=H, R′=Ac) which on acetylation proved identical with that obtained pre-

viously. That the reduction was stereoselective and specific was shown by treatment of the trione (VIII) under identical conditions. The product after acetylation was the 3β-acetate (XI), showing that only the 3-oxo group had been reduced to the 3β-hydroxyl. When larger quantities of the reagent were used the main product isolated was the 3β,7β-diacetate (XII), showing that the 7-oxo group was also reduced preferentially to the equatorial alcohol (cf. Shoppee and Summers 1950).



The first attempt to prepare VII (R=R′=Ac) was aimed at selectively ketalizing the 3-oxo group of V (R=Ac) followed by reduction of the 7-oxo group. However during the ketalization reaction, elimination of the axial 11β-acetoxy group occurred to give the ketal (XIII) after rearrangement. The structure of XIII followed from the ultraviolet absorption which showed the presence of an unsaturated ketone and on regeneration of the 3-carbonyl the known XIV was

obtained. Eventually the desired VII (R=R′=Ac) was obtained from the trione (VIII). Selective ketalization of the 3-oxo group gave the monoketal (XV) which was reduced by lithium aluminium hydride to a diol. Acetylation catalyzed by toluene-*p*-sulphonic acid again removed the protecting group to give the diacetate (VII; R=R′=Ac). The stereochemistry of the hydroxy groups follows from analogy (see above).

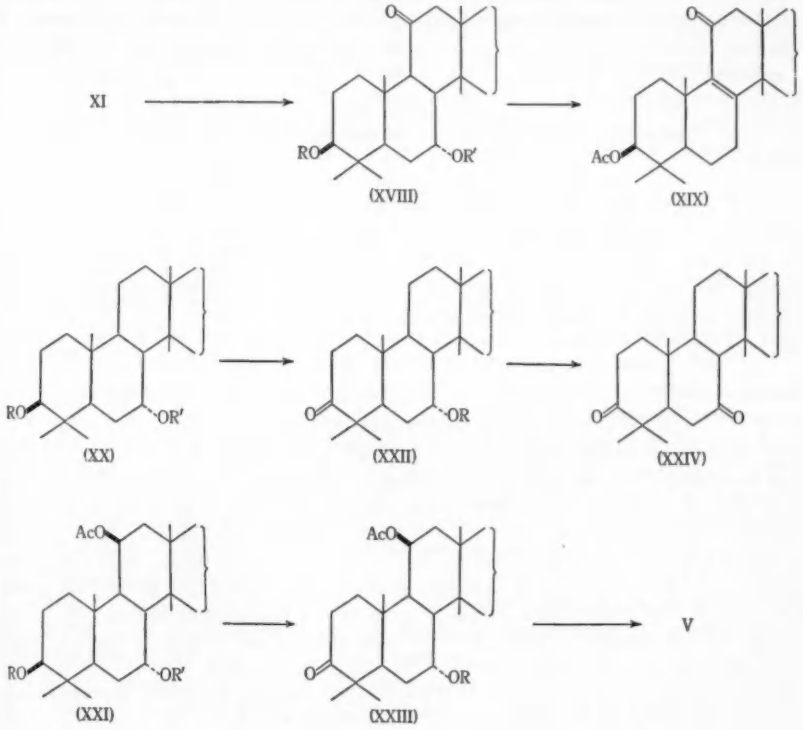
The results of hydrolysis experiments using 0·3N ethanolic potassium hydroxide are summarized in Figure 2. When two carbonyls were present as in V (R=Ac) the 11β-acetate was hydrolysed at a rate such that 90 per cent. had reacted in 2 hr. Crystals of the hydroxy compound then began to deposit and subsequent values were erratic. Hydrolysis was confirmed by isolation of the hydroxy compound, and dehydration to the ene-dione (XIV). When only one carbonyl was present as in VI and VII, it exerted a significant effect only when in the 7-position. Thus the 11β-acetoxy group of VI (R=H, R′=Ac) was over 40 per cent. hydrolysed in 3 hr. The single oxo group in the 3-position was ineffective under the conditions used. Thus VII (R=H, R′=Ac) with a 3-carbonyl was hydrolysed no quicker than II (R=H, R′=Ac) with no carbonyls.

To determine whether the 3-oxo group was producing an effect which was too slight to be detected under the mild conditions used to this stage, 11β-acetoxylanostan-3-one (XVII) was prepared. Voser *et al.* (1950) made a 3-acetoxylanostan-11-ol by acetylation of the product of lithium aluminium hydride reduction of 3-hydroxylanostan-11-one. By the method of formation and the inertness of the 11-hydroxy group to acetylation, this must be formulated as 3β-acetoxylanostan-11β-ol (XVI; R=H). Repetition of this experiment but using acid-catalysed acetylation of the product gave the diacetate (XVI; R=Ac). This was hydrolysed with 5 per cent. methanolic potassium hydroxide, and the product without purification oxidized to give an oxoacetate, which must be 11β-acetoxylanostan-3-one (XVII). Treatment of this 11β-acetate with N methanolic potassium hydroxide under reflux for 3 hr gave insignificant hydrolysis, as shown by the ease of elution of the product from alumina and recovery as starting material. We must conclude that the 3-oxo group alone is insufficient to facilitate hydrolysis of an 11β-acetate.

II. Hydrolysis of 7α-Acetates

In the steroid series where C_{14} is unsubstituted, an axial 7α-hydroxyl or acetoxyl behaves normally to esterification or hydrolysis. However, in the lanosterol series where C_{14} has an axial-methyl substituent, the 7α-substituent (Z, Fig. 1) is also axial and bears a *cis*-1,3-relationship to it, and is significantly more hindered. One demonstration of this is the relatively slow esterification of the 7α-hydroxyl. Barnes and Palmer (1957) isolated a hydroxy oxoacetate after acetylation of the reduction product from the 7,11-dione (XI). Because the hydroxyl survived the acetylating conditions the compound was tentatively regarded as VI (R=Ac, R′=H). It is now shown to be 3β-acetoxy-7α-hydroxylanostan-11-one (XVIII; R=Ac, R′=H). Dehydration gave the enone XIX, having a characteristic absorption spectrum and rotation. On more vigorous acetylation, the diacetate (XVIII; R=R′=Ac) was obtained, and hydrolysis

followed by benzoylation gave the dibenzoate (XVIII; R=R′=Bz), both of which had been obtained previously (Barnes and Palmer 1957). It follows that the structure XVIII (R=Ac, R′=H) is correct and that the 7α-hydroxy group had escaped acetylation, presumably because of hindrance from the 14α-methyl group. Finally, the 7α-hydroxy compound was prepared directly from 3β-acetoxylanostan-7,11-dione (XI) by reduction with Raney nickel at elevated temperature and pressure. It would be expected from Barton's (1953) generalizations that rapid reduction of the 7-oxo group would result in the formation of an axial hydroxyl.



A further demonstration of the hindrance of the 7α-substituent comes from hydrolysis of the 3β,7α-diacetate (XX; R=R′=Ac) (Barton and Thomas 1953) and the 3β,7α,11β-triacetate (XXI; R=R′=Ac) (Barnes and Palmer 1957). Even with 5 per cent. methanolic potassium hydroxide only one acetoxyl of each is hydrolysed to give hydroxy acetates which must be XX (R=H, R′=Ac) and XXI (R=H, R′=Ac). Presence of the hydroxy function was shown by chromium trioxide oxidation to the oxoacetates XXII (R=Ac), and XXIII (R=Ac) respectively. It was then found that the 7α-acetoxy group of

these oxoacetates could be easily hydrolysed to give hydroxy ketones, the structures of which were confirmed by oxidation to the known diones, XXIV (Barton and Thomas 1953) and V (R=Ac), respectively. A similar activation but by an 11-carbonyl function follows from the ease with which XVIII (R=R′=Ac) gives the diol (XVIII; R=R′=H) (Barnes and Palmer 1957).

Some of these 7α-acetoxy compounds were hydrolysed under the same conditions used for the quantitative study of the 11β-acetates, and the results are presented in Table 1. It is seen that with the non-ketonic 7α-acetate (XXI; R=R′=Ac), after the first group (3β) is hydrolysed the reaction becomes very slow. On the other hand, when an oxo group is in the 3-position, as in XXIII (R=Ac), or the 11-position as in XVIII (R=R′=Ac), the 7α-acetate is hydrolysed in less than 2 hr. Again the 3-oxo group has only a slight effect on the 11β-acetate (XXIII; R=H).

TABLE 1

HYDROLYSIS OF 7α-ACETATES IN 0·3N ETHANOLIC POTASSIUM HYDROXIDE

Lanostane Substituents	No. of Acetoxyls Hydrolysed in	
	1 Hr	2 Hr
3β,7α,11β-Triacetoxy-XXI (R=R′=Ac)	—	1·2
7α,11β-Diacetoxy-3-oxo-XXIII (R=Ac)	0·8	1·0
11β-Acetoxy-7α-hydroxy-3-oxo-XXIII (R=H) ..	—	0·2
3β,7α-Diacetoxy-11-oxo-XVIII (R=R′=Ac) ..	2·0	—

III. DISCUSSION

It is well established that electronegative substituents in either the alkyl or more effectively in the acyl component of an ester may cause an increase in the rate of hydrolysis (for discussion see Hammett 1940). However in the case of carbonyl activation, the relative rates of hydrolysis of the ethyl esters, $CH_3CH_2CO_2Et$, CH_3COCO_2Et, and $CH_3COCH_2CO_2Et$, are 0·553, 10000, and 2·66. The very large reduction in rate produced by one intervening methylene group renders it improbable that the carbonyls, which are separated from the alkyl oxygen by a chain of at least three carbon atoms in the present examples, could be exerting a facilitating inductive or transannular field effect. In the bile acid series an oxo group at the 12-position may possibly facilitate the hydrolysis of an 11β-acetate. Gallagher and Long (1946) have shown that methyl 3α,11β-diacetoxy-12α-hydroxycholanate (XXV; R=α-OH) has an 11β-acetoxyl which is resistant to hydrolysis after 3 hr in refluxing 0·6N aqueous-ethanolic potassium hydroxide. On the other hand, it was claimed (Long and Gallagher 1946) that the 11β-acetoxy group of the 12-oxo derivative (XXV; R=O) was hydrolysed at 0 °C with 0·6N potassium hydroxide. This result is difficult to interpret because no product was purified, or analysed, nor was the uptake of alkali measured. It is not regarded as analogous to the present examples of facilitation because in an α-acetoxyketone system it is difficult to distinguish between polar or electronic effects and because isomerization may occur.

In some cases of facilitation of hydrolysis of hindered ester groupings an intramolecular cyclic transition state between the ester and the activating group has been postulated. Henbest and Lovell (1957) have observed the more hindered 3α-(axial)-acetoxyl of an *allo*steroid to be hydrolysed more readily than the 3β-(equatorial)-acetoxyl when a 5α-hydroxyl is present. A cyclic hydrogen-bonded intermediate was postulated (cf. Bartlett and Greene 1954). Djerassi and Lippman (1955) suggested that a hemiacetal type cyclic transition state could explain in one example the facilitation of hydrolysis of a heavily hindered methoxycarbonyl group by a γ-carbonyl, although they recognized that this was unlikely for steric reasons.* In our present examples, the activating group lies on the opposite side of a *trans*-fused ring pair and no such intramolecular cyclic transition state is possible.

Heymann and Fieser (1951) (cf. Mattox *et al.* 1948) found that 11β-acetates of the bile acid series could be hydrolysed when a 3–9 oxygen bridge was present. They attributed the ease of hydrolysis to a neighbouring group participation. Again there is no analogy with the present work where there is no substituent adjacent to the acetoxyl.

Electrostatic effects could influence the rate of hydrolysis. However when the ethyl adipate anion is hydrolysed, the rate is less than one-half that of diethyl adipate (Ingold 1931), since the electrostatic effect produced by the anion works against the approach of the reagent. Similarly, an electrostatic effect produced by the enolate ion of the carbonyl group would retard the hydrolysis of the esters. On this basis the carbonyl must be exerting its effect in the non-ionized form.

Barton (1955; see also Barton, Head, and May 1957) has drawn attention to long-range effects operating in fused ring systems. Forty-threefold variations in the rate of reaction of triterpenoid 3-ketones with benzaldehyde were found depending on the presence of unsaturated functions in distant parts of the molecule. Since these results could not be explained on the basis of electrostatic or inductive effects the concept of conformational transmission was introduced. It was suggested that the unsaturated centres produced distortions of the ring system which were transmitted by an alteration of atomic coordinates and flexing of valence angles. It seems that similar arguments must apply in the present cases of facilitation of hydrolysis of the hindered acetoxyls. Corey and Sneen (1955) have shown by vector analysis that the carbonyl group of *cyclo*hexanone may cause some distortion of the chair ring. If this is transmitted to the adjacent ring so as to remove some of the hindrance from the acetoxyl either by reducing the axial character of it or of its hindering methyls, then approach of the reagent is possible, and hydrolysis may occur. That the proposed distortion is not transmitted through three fused rings is shown by the inability of the 3-oxo group alone to influence the 11β-acetoxy group as in compounds VII (R=H, R′=Ac) and XVII. However, when another oxo group is in the central ring as is the 7-oxo group of V (R=Ac) the effect of the 3-oxo group

* *Note added in Proof (October 1, 1958).*—Recently Djerassi and Mills (1958; *J. Amer. Chem. Soc.* **80**: 1236) have shown that this unexpected transition state is possible, since a lactone may be formed with ease from 21β-hydroxyoleanolic acid derivatives.

becomes apparent. The hydrolysis is then more rapid than when a 7-oxo group alone is present as in VI (R=H, R′=Ac). Presumably the conformational effect produced by the 3-oxo group is relayed and enhanced by the 7-oxo group.

It seems likely that the overall hindrance at the 7-position is reduced by a carbonyl at the 11-position. 3β,7β-Diacetoxylanostane (IV) is hydrolysed considerably more slowly than 3β-acetoxylanostane (III) in the presence of the same ratio of alkali to acetoxy groups (Fig. 2). Hence the 7β-position must be more hindered than the 3β-position. Now when 3β,7β-diacetoxylanostan-11-one (XII) was treated under identical conditions, it was hydrolysed completely in 15 min ; that is, at about the same rate as the monoacetate (III).

TABLE 2

MOLECULAR ROTATION DIFFERENCES ON EPIMERIZATION OF 7-ACETOXYLS

Substituents on Parent Lanostane	$[M]_D$ 7-Acetoxyl		Δ	Reference
	α	β		
3β-Acetoxy-11-oxo- ..	+ 60°	+315°	+255°	Cavalla and McGhie (1951) ; Barnes and Palmer (1957)
3-Oxo-11β-acetoxy- ..	— 60	+228	+288	Experimental
3β-Acetoxy-	—106	+175	+281	Barton and Thomas (1953)
3β,11β-Diacetoxy- ..	+100	+359	+259	Barnes and Palmer (1957)
3β,11α-Diacetoxy- ..	—106	+176	+282	

TABLE 3

MOLECULAR ROTATION DIFFERENCES ON EPIMERIZATION OF 11-ACETOXYLS

Substituents on Parent Lanostane	$[M]_D$ 11-Acetoxyl		Δ	Reference
	α	β		
3,7-Dioxo-	—30°	+135°	+165°	Experimental
3β-Acetoxy-7-oxo- ..	+163	+348	+185	Mijovic *et al.* (1952) ; experimental
3β-Acetoxy-	+127*	+344	+217	Experimental
3β,7α-Diacetoxy- ..	—106	+100	+206	Barnes and Palmer (1957)
3β,7β-Diacetoxy- ..	+176	+359	+183	

* Mijovic *et al.* (1952) report $[\alpha]_D$ +13° for this compound ; present work $[\alpha]_D$ +24°.

It might be expected that molecular rotation differences would be influenced by such profound conformational effects. Barton and Head (1956) could find no correlation between rotation effects and reaction rates in the mutarotation of steroidal 5,6-dibromides. Again, in the present work the rotation differences are similar in all cases. For example, Tables 2 and 3 show the change on epimerization of acetoxyls at the 7- and 11-positions of lanostane derivatives. In each case the values for compounds with hydrolysable hindered acetoxyls are similar to the rest of the series.

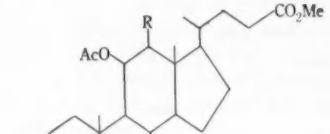
In the pentacyclic triterpenoid series, an angular methoxycarbonyl group at the 17-position, as in oleanolic acid methyl ester, is axial with respect to ring *D* and with a few exceptions requires exceptionally vigorous conditions to be hydrolysed. In those cases where hydrolysis occurs at the refluxing temperature of the usual solvents there is a carbonyl in rings *C*, *D*, or *E*, or in one case an hydroxyl group in ring *D*.

For ring *C* carbonyl compounds Ruzicka, Leuenberger, and Schellenberg (1937) and Ruzicka *et al.* (1938) have shown that while methyl oleanonate (3-oxo-Δ^{12}-XXVI) was not saponified by refluxing N potassium hydroxide solution, the methyl esters of oxoacetyldihydro-oleanolic acid (3β-acetoxy-12-oxo-XXVI), oxo-oleanolic acid (3β-hydroxy-11-oxo-Δ^{12}-XXVI), and *iso*-oxoacetyloleanolic acid (3β-acetoxy-12-oxo-$\Delta^{9(11)}$-XXVI) could be more than 50 per cent. saponified under the same conditions. It was noticed that when the carbonyl group was sufficiently far away from the methoxycarbonyl group, as in ring *A* (3-oxo-Δ^{12}-XXVI), then hydrolysis was not facilitated. Likewise in our examples, the isolated 3-oxo group was found to be ineffective in facilitating the hydrolysis of the 11β-acetate (e.g. VII, XVII, and XXIII). Activation is achieved by a carbonyl at the 16-position in ring *D*, as in the echinocystic acid derivative (3β-hydroxy-11,16-dioxo-Δ^{12}-XXVI) (Ruzicka, Nisoli, and Jeger 1946) and the quillaic acid derivative (3,16-dioxo-Δ^{12}-23-norXXIV) (Elliott, Kon, and Soper 1940). When the carbonyl is in ring *E*, hydrolysis is possible with several derivatives of siaresinolic acid (Bilham, Kon, and Ross 1942) having a 19-oxo group, with methyl machaerate (3β-hydroxy-21-oxo-Δ^{12}-XXVI) (Djerassi and Lippmann 1955), and with the oleanolic acid derivative (3β-acetoxy-12,19-dioxo-$\Delta^{9(11),13(18)}$-XXVI) (Kon and Ross 1942).

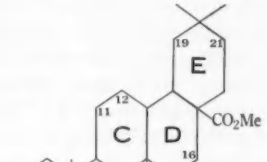
Other examples of "carbonyl facilitation" come from the glycyrrhetic acid field. Glycyrrhetic acid has been shown by Beaton and Spring (1955) to have an axial carboxy group. Ruzicka, Leuenberger, and Schellenberg (1937) showed that while glycyrrhetic acid methyl ester (XXVII) may be saponified with refluxing 0·5N ethanolic potassium hydroxide, the 11-deoxy compound is resistant to these conditions.

In each of the examples mentioned so far hydrolysis of the axial methoxycarbonyl group may be considered as being due to loss of axial character by distortion of the ring system by carbonyls in the vicinity. It might be expected on this argument that a facilitation could be achieved if a similar distortion were produced by ethylenic bonds (cf. Barton, Head, and May 1957). Although we know of no analogous hydrolysis reactions, Wendler *et al.* (1957) have shown that double bonds in ring *C* of a steroid may allow acetylation of an 11β-hydroxy group under conditions in which the saturated compound would not react. Presumably this is due to removal of hindrance by distortion (Corey and Sneen 1955) affecting the relative positions of the hydroxyl and *cis*-methyl groups. On the other hand, a Δ^7-compound could not be acetylated under similar conditions (Bladon *et al.* 1953). This suggests that in our examples the carbonyl groups are not facilitating hydrolysis by conformational effects produced through the double bond of the enol, for with a 7-oxo-11β-acetoxy compound enolization would be expected to give a double bond at the 7-position.

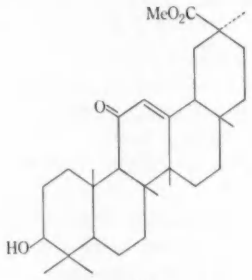
Djerassi and Monsimer (1957) found that methyl cochalate (3β, 16β-dihydroxy-Δ^{12}-XXVI) is hydrolysed slowly by refluxing 10 per cent. methanolic potassium hydroxide. In this case a six-membered cyclic transition state between the hydroxyl and *cis*-methoxycarbonyl groups similar to that demonstrated by Henbest and Lovell (1957) is possible, and may account for the hydrolysis. It would be interesting to compare methyl echinocystate (i.e. methyl-16-*epi*cochalate) under the same conditions. Here the hydroxyl is *trans* to the methoxycarbonyl and no cyclic transition state is possible. Bergsteinsson and Noller (1934) do in fact report on the difficulty of saponifying methyl echinocystate, but under unspecified conditions.



(XXV)



(XXVI)



(XXVII)

IV. Experimental

(*a*) *General*

Melting points are corrected, and taken in open capillary tubes unless otherwise stated. Analyses are by Dr. K. W. Zimmermann, C.S.I.R.O. Microanalytical Laboratory at the University of Melbourne. All rotations were measured at 20±2 °C in chloroform solution at a concentration of 1–2 per cent. using the sodium D-line. The absorption spectra were measured in ethanol solution. Light petroleum refers to the fraction b.p. 60–80 °C.

(*b*) *Rates of Hydrolysis*

These were determined using a weight of compound such as to give equimolar parts of acetoxyls, based arbitrarily on 3β,7β-diacetoxylanostane (100 mg). To the sample in a 25 ml round-bottom flask was added 0·3N ethanolic potassium hydroxide (5·0 ml) and the solution

heated under reflux with protection against carbon dioxide. After the required time, excess alkali was titrated with 0·1N hydrochloric acid and the results calculated in terms of number of acetoxyls hydrolysed, as in Figure 2 and Table 1.

(c) *11β-Acetoxylanostane-3,7-dione (V; R=Ac) and Reactions*

(i) The triacetate (II; R=R′=Ac) (1 g) was hydrolysed by treatment with refluxing 5% methanolic potassium hydroxide (200 ml) for 1 hr. Crystallization from acetone-water gave *11β-acetoxylanostane-3β,7β-diol (II; R=H, R′=Ac)*, m.p. 156 °C, $[\alpha]_D$ +60° (Found after drying under reduced pressure over P_2O_5: C, 74·4; H, 11·1%. Calc. for $C_{32}H_{56}O_4.\frac{1}{2}H_2O$: C, 74·8; H, 11·2%). Treatment of the diol (50 mg) with benzoyl chloride (0·5 ml) in pyridine (1 ml) on the steam-bath for 1 hr, gave the *dibenzoate (II; R=Bz, R′=Ac)* which crystallized from chloroform-methanol to have m.p. 233–235 °C, $\lambda_{max.}$ 230 mμ, ε 29,000 (Found: C, 77·9; H, 9·2%. Calc. for $C_{46}H_{64}O_6$: C, 77·5; H, 9·1%). The diol (II; R=H, R′=Ac) (500 mg) was dissolved in chloroform-acetic acid (50 ml) and a solution of chromium trioxide (400 mg) in water (2 ml) added. After standing 2 hr at room temperature the product was isolated and crystallized from chloroform-methanol to give *11β-acetoxylanostane-3,7-dione (V; R=Ac)*, m.p. 177–178 °C, $[\alpha]_D$ +27° (Found: C, 76·7; H, 10·7%. Calc. for $C_{32}H_{52}O_4$: C, 76·7; H, 10·5%).

(ii) *Hydrolysis.*—The acetate (V; R=Ac) (200 mg) was hydrolysed in refluxing 0·3N ethanolic potassium hydroxide (5 ml) for 2 hr. Crystallizations from chloroform-methanol gave *11β-hydroxylanostane-3,7-dione (V; R=H)*, m.p. 240–241 °C, $[\alpha]_D$ +36° (Found: C, 78·7; H, 11·0%. Calc. for $C_{30}H_{50}O_3$: C, 78·5; H, 10·9%).

(iii) *Elimination Reactions.*—(1) The hydroxy compound V (R=H) (100 mg) was dissolved in acetic acid (10 ml) and perchloric acid (72%; 2 drops) added. After standing on the steam-bath for 30 min the product was isolated and had m.p. 145–147 °C, $[\alpha]_D$ +19°, $\lambda_{max.}$ 254 mμ, ε 12,600 in good agreement with the constants given by Cavalla, McGhie, and Pradhan (1951) for lanost-8-ene-3,7-dione (XIV).

(2) The dioxoacetate (V; R=Ac) (600 mg) was treated with ethylene glycol (85 mg) in refluxing benzene (40 ml) with azeotropic removal of water, using toluene-*p*-sulphonic acid (240 mg) as catalyst. After 5 hr the solution was worked up and the product crystallized from chloroform-methanol to give *3,3-ethylenedioxylanost-8-en-7-one (XIII)*, m.p. 219–221 °C, $[\alpha]_D$ —7°, $\lambda_{max.}$ 254 mμ, ε 9,000 (Found: C, 79·4; H, 10·8%. Calc. for $C_{32}H_{52}O_3$: C, 79·3; H, 10·8%). The monoketal (XIII) was dissolved in acetic acid, dilute sulphuric acid added, and stood on the steam-bath for 15 min. A few drops of water were added, the solution cooled, and the resulting lanost-8-ene-3,7-dione (XIV) had m.p. 149–150 °C, undepressed with that above and with similar rotation and ultraviolet absorption.

(iv) *Reduction.*—The acetate (V; R=Ac) (2 g) was dissolved in methanol (350 ml) and sodium borohydride (200 mg) dissolved in methanol (20 ml) was added to the ice-cold solution with shaking. After 2 hr at 0 °C, acetic acid (5 ml) was added, the solution concentrated, and the product isolated. After purification by chromatography the product crystallized from chloroform-methanol to give 3β-hydroxy-11β-acetoxylanostan-7-one (VI; R=H, R′=Ac), m.p. 197–198 °C, $[\alpha]_D$ +80° (Found: C, 76·3; H, 10·8%. Calc. for $C_{32}H_{54}O_4$: C, 76·4; H, 10·8%). Acetylation with acetic anhydride-pyridine overnight at room temperature gave *3β,11β-diacetoxylanostan-7-one (VI; R=R′=Ac)*, m.p. 219–221 °C, $[\alpha]_D$ +64° m.p. undepressed by material obtained previously (Barnes and Palmer 1957) (Found: C, 75·4; H, 10·3%. Calc. for $C_{34}H_{56}O_5$: C, 75·0; H, 10·4%).

(d) *Ketals of Lanostane-3,7,11-trione (VIII) and their Reactions*

(i) *Monoketal.*—The trione (VIII) (961 mg), toluene-*p*-sulphonic acid (379 mg), and ethylene glycol (146 mg) were reacted in refluxing benzene (50 ml) for 5 hr with azeotropic distillation of water. After working up, the product crystallized from chloroform-methanol to give *3,3-ethylenedioxylanostane-7,11-dione (XV)*, m.p. 211–213 °C (Found: C, 77·0; H, 10·6%. Calc. for $C_{32}H_{52}O_4$: C, 76·7; H, 10·5%). Reduction of the monoethylene ketal (XV) (2 g) by lithium aluminium hydride (500 mg) in refluxing ether (200 ml) for 2 hr gave a product showing no carbonyl absorption in the infra-red ("Nujol mull"). Acetylation of the total product with

acetic anhydride–toluene-*p*-sulphonic acid gave a product showing no hydroxyl absorption, but having bands at 1730 cm^{-1} (acetate) and 1690 cm^{-1} (carbonyl) in a " Nujol mull ". Chromatography over alumina gave the main fractions, eluted with benzene, which crystallized from methanol to give *7β,11β-diacetoxylanostan-3-one* (*VII ; R=R'=Ac*), m.p. 214–217 °C (sealed tube), $[\alpha]_D$ +42° (Found : C, 75·2 ; H, 10·4%. Calc. for $C_{34}H_{56}O_5$: C, 75·0 ; H, 10·4%).

(ii) *Diketal.*—The trione (VIII) (800 mg), toluene-*p*-sulphonic acid (500 mg), and ethylene glycol (800 mg) were treated as above to give *3,3,7,7-di(ethylenedioxy)lanostan-11-one* (*IX*). Crystallizing from chloroform-methanol, m.p. 183–185 °C (Found : C, 75·1 ; H, 10·3%. Calc. for $C_{34}H_{56}O_5$: C, 75·0 ; H, 10·4%). Reduction in the usual way with lithium aluminium hydride in ether gave *3,3,7,7-di(ethylenedioxy)lanostan-11β-ol* (*X*), crystallizing from chloroform-methanol to have m.p. 180–182 °C (depressed to 170–175 °C on mixing with starting material). The hydroxy compound (X) was acetylated by standing overnight with acetic anhydride–toluene-*p*-sulphonic acid at room temperature. The acetate had m.p. 175–177 °C undepressed on mixing with 11β-acetoxylanostane-3,7-dione from Section IV(*c*).

The diketal (IX) (300 mg) was dissolved in ether (5 ml) and dioxan (5 ml) and added to liquid ammonia (50 ml) and methanol (5 ml). Lithium (1 g) was added in small portions to the stirred suspension and after the blue colour became persistent, ammonium chloride (5 g) was added. After evaporation of the ammonia the solid was extracted with ether, and a trace of unreacted ketone was removed by benzene elution from alumina. The strongly absorbed fraction was acetylated by heating for 2 hr with acetic anhydride-acetic acid and gave on crystallization from chloroform-methanol, *3,3,7,7-di(ethylenedioxy)lanostan-11α-yl acetate*, m.p. 183–185 °C, $[\alpha]_D$ −20° (Found : C, 73·7 ; H, 10·4%. Calc. for $C_{36}H_{60}O_6$: C, 73·4 ; H, 10·3%).

The diketal was hydrolysed by warming with toluene-*p*-sulphonic acid on the steam-bath for 15 min. Crystallization from methanol-water gave *11α-acetoxylanostan-3,7-dione*, m.p. 148–149 °C, $[\alpha]_D$ −6° (Found : C, 76·9 ; H, 10·5%. Calc. for $C_{32}H_{52}O_4$: C, 76·7 ; H, 10·5%).

(*e*) *7α-Acetoxylanostan-3-one* (*XXII ; R=Ac*)

The diacetate (XX ; R=R'=Ac) (300 mg) was treated for 1 hr with refluxing 5% methanolic potassium hydroxide (50 ml), and worked up to give an uncrystallizable monohydroxyacetate (Found : C, 78·7 ; H, 11·6%. Calc. for $C_{32}H_{56}O_3$: C, 78·6 ; H, 11·6%), which (200 mg) was dissolved in acetic acid and oxidized at room temperature for 7 hr with chromium trioxide (44 mg). Filtration of the product through alumina and crystallization from methanol-water gave *7α-acetoxylanostan-3-one* (*XXII ; R=Ac*), m.p. 148–149 °C, $[\alpha]_D$ −40° (Found : C, 79·0 ; H, 11·3%. Calc. for $C_{32}H_{54}O_3$: C, 79·0 ; H, 11·2%). The oxoacetate (XXII ; R=Ac) (100 mg) was hydrolysed in the usual way for 1 hr with 5% methanolic potassium hydroxide (50 ml). Crystallization of the product from ethanol-water gave *7α-hydroxylanostan-3-one* (*XXII ; R=H*), m.p. 145–146 °C, $[\alpha]_D$ +18° (Found after drying under reduced pressure over P_2O_5 : C, 79·2 ; H, 11·3%. Calc. for $C_{30}H_{50}O_2 \cdot \frac{1}{2}H_2O$: C, 79·4 ; H, 11·8%). Oxidation of the hydroxy ketone (50 mg) with chromium trioxide (25 mg) in acetic acid (10 ml) gave lanostane-3,7-dione, m.p. 130–131 °C, $[\alpha]_D$ +3°, and correct analysis.

(*f*) *7α,11β-Diacetoxylanostan-3-one* (*XXIII ; R=Ac*) *and Reactions*

3β-Acetoxylanostane-7,11-dione (XI) (40 g) was reduced by refluxing overnight in diethylene glycol in the presence of the corresponding sodium alkoxide (Barnes and Palmer 1957). The product was reduced by lithium aluminium hydride (10 g) in refluxing ether (800 ml) for 2 hr to complete the reduction of the 11-oxo group to an 11β-hydroxyl. The product from this reaction was acetylated by first treating with acetic anhydride and acetic acid at 100 °C for 1 hr then by adding toluene-*p*-sulphonic acid (1 g) to the cooled solution. The product was again worked up and then hydrolysed in a large volume (2 l.) of methanol and dioxan to which potassium hydroxide (50 g) in water (50 ml) was added. After working up, the product was expected to consist mainly of the diol, 11β-acetoxylanostane-3β,7β-diol, and the monohydric alcohol, 7α,11β-diacetoxylanostan-3β-ol. The mixture was then chromatographed over alumina and 20 fractions obtained on elution with ether. From these were obtained crystals (2 g) from methanol, which on recrystal-

lization gave *7α,11β-diacetoxylanostan-3β-ol* (*XXI ; R=H, R′=Ac*), m.p. 279–284 °C, $[\alpha]_D$ +22° (Found : C, 74·8 ; H, 10·7%. Calc. for $C_{34}H_{58}O_5$: C, 74·8 ; H, 10·6%). On acetylation with acetic acid-acetic anhydride the 3β,7α,11β-triacetate was obtained having m.p. 234–237 °C (242–245 °C sealed tube) undepressed in both instances with authentic material (Barnes and Palmer 1957).

The hydroxy compound (XXI ; R=H, R′=Ac) (1 g) was dissolved in acetic acid (50 ml) and chromium trioxide (200 mg) in acetic acid (10 ml) added. After standing overnight, working up, and filtering through alumina, *7α,11β-diacetoxylanostan-3-one* (*XXIII ; R=Ac*) was obtained ; it crystallized from chloroform-methanol to have m.p. 221–224 °C, $[\alpha]_D$ —11° (Found : C, 74·6 ; H, 10·3%. Calc. for $C_{34}H_{56}O_5$: C, 75·0 ; H, 10·4%).

(i) *Hydrolysis.*—The oxodiacetate (XXIII ; R=Ac) (204·5 mg) was treated with refluxing 0·3N potassium hydroxide in ethanol (5·00 ml) for 2 hr 18 min and the excess alkali titrated to show that 1·00 acetoxyls had hydrolysed. Working up and crystallizing from light petroleum-methanol gave *11-β-acetoxy-7α-hydroxylanostan-3-one* (*XXIII ; R=H*), m.p. 180–183 °C, $[\alpha]_D$ +33° (Found : C, 76·5 ; H, 10·8%. Calc. for $C_{32}H_{54}O_4$: C, 76·4 ; H, 10·8%). Oxidation with chromium trioxide-acetic acid of the hydroxy compound (XXIII ; R=H) gave 11β-acetoxylanostane-3,7-dione (V ; R=Ac) having m.p. 176–178 °C undepressed on mixing with an authentic sample.

(g) 3β-Acetoxy-7α-hydroxylanostan-11-one (*XVIII ; R=Ac, R′=H*)

3β-Acetoxylanostane-7,11-dione (XI) (500 mg) was dissolved in ethanol (50 ml) and reduced with hydrogen in presence of Raney nickel (1 g) at 200 °C and 2000 p.s.i. for 3 hr. The fraction strongly absorbed on alumina (400 mg) was crystallized from chloroform-methanol to have m.p. 252–257 °C, $[\alpha]_D$ +41° and shown to be XVIII (R=Ac, R′=H) by acetylation (acetic anhydride–toluene-*p*-sulphonic acid) and comparison with the infra-red spectrum of Section IV(*h*).

(h) Reactions of 3β-Acetoxy-7α-hydroxylanostan-11-one (*XVIII ; R=Ac, R′=H*)

(i) *Dehydration.*—The hydroxy compound (XVIII ; R=Ac, R′=H) (100 mg) was dissolved in acetic acid (20 ml) and perchloric acid (6 drops) added. The solution was stood on the steam-bath for 30 min and worked up. Filtration of a benzene solution of the product through alumina gave 3β-acetoxylanost-8-en-11-one (XIX) which crystallized from chloroform-methanol to have m.p. 132–133 °C, $[\alpha]_D$ +157°, $\lambda_{max.}$ 255 mμ, ε 8000 and the correct analysis. (Mijovic *et al.* 1952 report similar values.)

The hydroxy compound (XVIII ; R=Ac, R′=H) (100 mg) was dissolved in pyridine (5 ml), phosphorus oxychloride (1 ml) added, and the solution stood overnight at room temperature. Working up in the usual way gave a product with properties similar to those above.

(ii) *Acetylation.*—The hydroxy compound (XVIII ; R=Ac, R′=H) (200 mg) was dissolved in acetic acid at 0 °C and acetic anhydride (15 ml) containing perchloric acid (1 drop) was added. The diacetate (XVIII ; R=R′=Ac) which analysed correctly, had m.p. 194–195 °C, $[\alpha]_D$ +10° and was undepressed on mixed m.p. with that obtained previously (Barnes and Palmer 1957).

(i) Reductions of Lanostane-3,7,11-trione (*VIII*) *by Sodium Borohydride*

(i) The trione (VIII) (1 g) was dissolved in methanol (200 ml) and cooled to 0 °C ; sodium borohydride (200 mg) was added and the solution kept at 0 °C for 2·5 hr. After adding acetic acid (5 ml), the product was acetylated with acetic anhydride-pyridine at 100 °C for 1 hr. Chromatography through alumina from light petroleum solution gave 3β-acetoxylanostane-7,11-dione (XI) having m.p. 218–220 °C, $[\alpha]_D$ +58°, m.p. undepressed on mixing with an authentic sample. Benzene eluted fractions (400 mg) which on crystallization from methanol had m.p. 175–176 °C, $[\alpha]_D$ +50°, m.p. undepressed on mixing with 3β,7β-diacetoxylanostan-11-one (XII) (Voser *et al.* 1950).

(ii) The trione (VIII) (1·1 g) was treated as above except that sodium borohydride (120 mg) was used and the time of reaction was reduced to 1 hr. Chromatography of the acetylated product gave only the dione (XI) as determined by mixed m.p. of the crystallized material.

(j) 11β-Acetoxylanostan-3-one (XVII)

3β-Acetoxylanostan-11-one (1 g) was reduced with lithium aluminium hydride in refluxing ether in the usual way, the product acetylated with acetic anhydride–toluene-*p*-sulphonic acid and chromatographed. Crystallization from chloroform-methanol gave *3β,11β-diacetoxylanostane* (*XVI*), m.p. 185–186 °C, $[\alpha]_D$ +72° (Found: C, 77·2; H, 11·1%. Calc. for $C_{34}H_{58}O_4$: C, 76·9; H, 11·0%). Hydrolysis of the diacetate (XVI) (400 mg) in refluxing 5% ethanolic potassium hydroxide for 2 hr gave a product which was dissolved in chloroform-acetic acid (10 ml) and oxidized with chromium trioxide (300 mg) in acetic acid-water (5 ml) for 2 hr. After filtering through alumina the product crystallized from chloroform-methanol to give *11β-acetoxylanostan-3-one* (*XVII*), m.p. 174–175 °C, $[\alpha]_D$ +43° (Found: C, 79·2; H, 11·1%. Calc. for $C_{32}H_{54}O_3$: C, 78·9; H, 11·2%). Treatment of the acetoxy ketone (XVII) by refluxing with 5% ethanolic potassium hydroxide for 4 hr and chromatographing over alumina, gave quantitative recovery of light petroleum eluted material which crystallized as the starting material.

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ALKALOIDS OF THE AUSTRALIAN RUTACEAE: *LUNASIA QUERCIFOLIA*

I. 7-METHOXY-1-METHYL-2-PHENYL-4-QUINOLONE

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Summary

Bark of *Lunasia quercifolia* contains *c.* 4–4·5 per cent. alkaloids consisting of *c.* 3–3·5 per cent. water-soluble bases and *c.* 1 per cent. tertiary bases. Three component tertiary bases have been isolated; these are the previously described alkaloids lunacrine and lunine and an undescribed base $C_{17}H_{15}O_2N$. This new base is shown by degradative processes and by synthesis to be 7-methoxy-1-methyl-2-phenyl-4-quinolone (I). The products of the action of nitric acid on the alkaloid include mono- and dinitro derivatives which undergo hydrolytic fission, giving rise to 2-methylamino-ω-nitroacetophenones.

I. INTRODUCTION

The only representative of the genus *Lunasia* known to occur in Australia is regarded as identical with the New Guinea species *L. quercifolia* (Warb.) Lauterb. et K. Schum.‡ *L. quercifolia* is closely allied to *L. amara*, a species from the Malayan archipelago which has been investigated chemically by several groups of workers, and it will be shown in the present paper that the Australian species also resembles *L. amara* in the general pattern of its alkaloid content. *L. quercifolia* occurs in Queensland in the Cape York peninsula north of Cooktown; it is a small tree about 10–15 ft in height. The bark and leaves of *L. amara* have been used medicinally and Atkinson (1956) finds the bark of the Australian species (reported as *L. amara*) to show pronounced antibacterial activity.

Several alkaloids have been isolated from the bark and leaves of *L. amara*; the early work is summarized by Henry (1949) and by Steldt and Chen (1943). The alkaloids of the leaves are currently being studied by Dr. E. C. Horning and Dr. S. M. Goodwin (see Goodwin, Smith, and Horning 1957) and because of the similarity of the two species the present work on *L. quercifolia* is to be concerned only with the alkaloids of the bark. The alkaloid content of the bark is of the order of 4–4·5 per cent., the alkaloids falling into two groups—those readily extractable from aqueous alkaline solution by chloroform (*c.* 1 per cent.) and those extractable only extremely slowly (*c.* 3–3·5 per cent.). For convenience

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the first group will be referred to as the " tertiary bases ", the second as the " water-soluble bases ". The water-soluble bases are very sensitive to alkali and it is advisable to keep the solution at a pH less than 9 during separation of the two groups and to extract as quickly as possible. Alkali converts the water-soluble bases to a mixture of weakly basic water-insoluble materials ; this mixture is obtained, for example, when the bark is treated with lime and then extracted with trichloroethylene. It is suggested that some of the substances isolated by earlier workers (e.g. the lunacridine described by Boorsma 1904) may be artefacts arising in this way.

Chromatography on buffered paper with water-saturated *iso*pentanol reveals the presence of at least five components in the water-soluble group ; extracts from specimens of the bark of authentic *L. amara** run in the same manner likewise show the presence of large amounts of the water-soluble bases. There are at least four components in extracts of *L. amara* bark and these correspond in R_F values with bases present in *L. quercifolia* extracts. On such chromatograms the tertiary base group appears near the solvent front ; *L. quercifolia* extracts also show two weak spots of high R_F value, one of which is detectable on chromatograms of *L. amara* bark extracts. Chromatograms of extracts of the leaves of *L. quercifolia* show the presence of four water-soluble bases corresponding in R_F values with four of five such bases observed on chromatograms of *L. amara* leaf extract. The latter, in addition, show at least one high R_F spot not demonstrable in *L. quercifolia* extracts. No really satisfactory system has been devised for separating the components of the tertiary base fraction but the use of buffered papers with a mixture of benzene-light petroleum as mobile phase shows two major spots with the tertiary bases of *L. quercifolia*. In fact, one of these represents two difficultly separable components ; there are also additional, very weak, spots due to minor components.

Three alkaloids have been isolated from the tertiary base fraction. The major component (*c.* 0·5–1 per cent.), $C_{16}H_{19}O_3N$, m.p. 117–118 °C, is clearly the lunacrine described by previous workers. It is accompanied by *c.* 0·05 per cent. of a base $C_{16}H_{17}O_4N$, m.p. 222–223·5 °C, evidently identical with Boorsma's lunine and *c.* 0·2 per cent. of a previously undescribed base $C_{17}H_{15}O_2N$, m.p. 199–200 °C, shown to be 7-methoxy-1-methyl-2-phenyl-4-quinolone (I). A further 0·2 per cent. of I can be obtained from the mixture resulting from treatment of the water-soluble bases with alkali ; the nature of the water-soluble component giving rise to I will be dealt with in a later paper. This circumstance, which may have some bearing on the variability of yields experienced, particularly with lunacrine, raises the possibility that the tertiary bases themselves may be artefacts. However, it has been shown chromatographically that bases characterized by R_F values the same as those of lunacrine and I are present in the *dried* plant. We have not yet had an opportunity to examine fresh material.

* One obtained from Dr. E. Quisumbing, to whom we are much indebted, with the help of Mr. W. J. Ellis of the United Nations Educational, Scientific, and Cultural Organization, the other through the kindness of Dr. Goodwin and Dr. Horning.

The similarity of I to 2-phenyl-4-methoxyquinoline isolated from *L. amara* by Goodwin, Smith, and Horning (1957) is noteworthy. Sondheimer and Meisels (1958) have recently shown that edulein, from the bark of the rutaceous plant *Casimiroa edulis*, is identical with I from *L. quercifolia*.

II. 7-Methoxy-1-methyl-2-phenyl-4-quinolone*

The alkaloid $C_{17}H_{15}O_2N$ forms mono and dibromo derivatives, but is resistant to attack by acids, alkalis, oxidizing, and reducing agents; it is not acetylated nor does it react with carbonyl reagents. It contains one methoxyl and one methylimino group; demethylation of the former gives a phenol from which the alkaloid may be regenerated. Infra-red absorption in the carbonyl region (1618 cm^{-1}; see Fig. 1) is in accord with a 4-quinolone structure (Price and Willis, unpublished data), and a band at 704 cm^{-1} is consistent with the

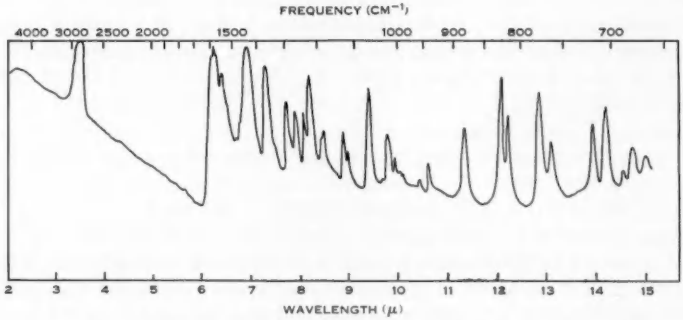


Fig. 1.—Infra-red spectrum of 7-methoxy-1-methyl-2-phenyl-4-quinolone ("Nujol mull").

presence of a monosubstituted benzenoid ring. The ultraviolet absorption (Fig. 2), likewise, is consistent with that for a 4-quinolone and differs from the characteristic 2-quinolone spectrum; there is little change in the ultraviolet spectrum in the presence of acid. The methiodide, formed by heating with methyl iodide at 100 °C, is decomposed at its melting point or by the action of alkali, to the parent base. The hydrochloride of the alkaloid is not demethylated by heating to 250 °C, consequently it is most unlikely that the methoxyl group is located *peri* to a quinolone carbonyl group.

Boiling 68 per cent. nitric acid converts the alkaloid to a mixture of benzoic acid, 3-hydroxy-2,4,6-trinitrophenylmethylnitramine (II) and the mono or dinitro derivatives of the alkaloid, depending on the reaction time. The nitro derivatives, as discussed below, undergo hydrolytic ring cleavage to benzoic acid and what are evidently ω-nitroacetophenones. These data, though not conclusive, indicate structure I for the alkaloid. The phenol $C_{16}H_{13}O_2N$ formed by demethylating the alkaloid is oxidized smoothly by nitric acid giving, after

* A preliminary account has been given by Price (1956).

decarboxylation, an acid $C_{13}H_{11}O_3N$, presumably 1-methyl-6-phenyl-4-pyridone-3-carboxylic acid (III).

Structure I has been established by synthesis. 4-Hydroxy-7-methoxy-2-phenylquinoline (V) has been synthesized by Elderfield *et al.* (1946) from

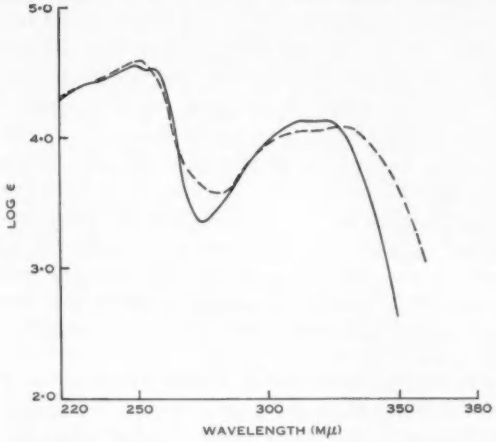
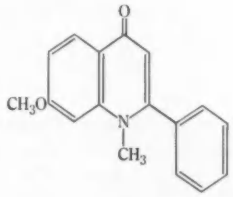
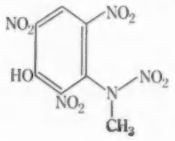


Fig. 2.—Ultraviolet spectrum of 7-methoxy-1-methyl-2-phenyl-4-quinolone.
—— In ethanol.
--- In ethanol containing 5 equiv. HCl.

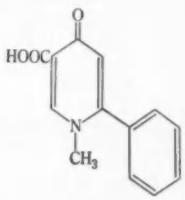
benz-*m*-anisidide by conversion to the chloroimide (IV) followed by condensation with malonic ester, saponification, and decarboxylation. The possibility that cyclization might have given rise to the alternative 5-methoxy compound had been eliminated by conversion of V to the 4-chloro compound followed by



(I)



(II)

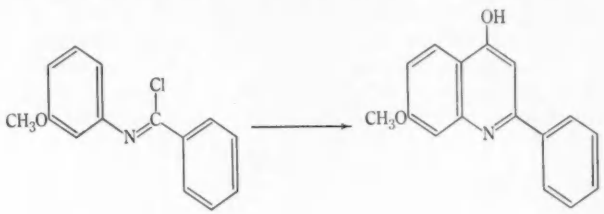


(III)

catalytic dehalogenation to authentic 2-phenyl-7-methoxyquinoline. Methylation of V with dimethyl sulphate and potassium hydroxide gives I identical with the naturally occurring alkaloid.

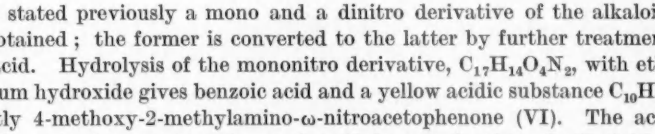
7-Methoxy-1-methyl-3-phenyl-4-quinolone has been synthesized for comparison from *m*-anisidine and ethyl formyl phenyl acetate following the procedure

of Adams and Hey (1950).* An attempt to synthesize V by the procedure of Fuson and Burness (1946)—heating acetophenone diethyl ketal with ethyl 2-amino-4-methoxybenzoate—was unsuccessful though, as reported by Fuson and Burness, the reaction proceeds smoothly with methyl anthranilate, methylation of the resulting 2-phenyl-4-quinolone giving 1-methyl-2-phenyl-4-quinolone for which we confirm the higher melting point reported by Goodwin, Smith, and Horning (1957). The ultraviolet absorption spectrum of 1-methyl-2-phenyl-4-quinolone closely resembles that of the alkaloid (I; see Fig. 2).



(IV) (V)

As stated previously a mono and a dinitro derivative of the alkaloid have been obtained; the former is converted to the latter by further treatment with nitric acid. Hydrolysis of the mononitro derivative, $C_{17}H_{14}O_4N_2$, with ethanolic potassium hydroxide gives benzoic acid and a yellow acidic substance $C_{10}H_{12}O_4N_2$, evidently 4-methoxy-2-methylamino-ω-nitroacetophenone (VI). The action of ethanolic potassium hydroxide on the dinitro derivative, $C_{17}H_{12}O_6N_3$, gives rise to two products in addition to benzoic acid. The major component,



(VI) (VII) (VIII)

$C_{11}H_{13}O_6N_3$, is presumably 4-ethoxy-2-methylamino-5(or 3)-nitro-ω-nitroacetophenone (VII), its formation involving ether interchange, and the second, $C_{10}H_{12}O_5N_2$, 4-ethoxy-2-methylamino-5(or 3)-nitrobenzoic acid (VIII). An ω-nitroacetophenone has not been obtained from reaction of either nitro derivative of I with methanolic potassium hydroxide; in each case the reaction proceeds further and the substances isolated are respectively 4-methoxy-2-

* The alternative structure, 5-methoxy-1-methyl-3-phenyl-4-quinolone can be excluded since (i) 7(or 5)-methoxy-3-phenyl-4-quinolone, from which it was obtained by methylation, is soluble in alkali, whereas 8-methoxy-1-naphthol is cryptophenolic, and (ii) the demethylation product, 7(or 5)-hydroxy-1-methyl-3-phenyl-4-quinolone, is also soluble in alkali—cf. the 2- and 4-hydroxy-10-methylacridones.

methylaminobenzoic acid, identified by comparison with a synthetic specimen and an acid, $C_9H_{10}O_5N_2$, evidently 4-methoxy-2-methylamino-5(or 3)-nitrobenzoic acid.

The infra-red spectrum of VI supports the structures allocated. The presence of an NH< group is shown by a band at 3335 cm^{-1} (NH stretching) both in solution (CCl_4) and in the solid state. The frequency is lower than would be expected in the absence of hydrogen bonding, and since there is no difference between the spectrum of the solid and that in solution, the hydrogen bonding must be intramolecular. A doublet at 1638 and 1623 cm^{-1} is consistent with the presence of a carbonyl group which, since the frequency is so low, must also be hydrogen bonded. Again there is little change on passing from solid to solution showing that the hydrogen bonding is intramolecular—compare *o*-aminoacetophenone (Jones, Forbes, and Mueller 1957). Bands at 1358 and 1562 cm^{-1} are due to a nitro group, not *necessarily* aliphatic, though 1562 cm^{-1} is rather high for an aromatic nitro group. However, the spectrum of ω-nitroacetophenone itself also contains a band at 1562 cm^{-1}. Furthermore, bands at 820 and 849 cm^{-1} are consistent with the presence of two adjacent unsubstituted carbon atoms in a benzenoid ring, and bands at 1023, 1067, 1128, 1171, and 1188 cm^{-1} suggest 1,2,4-trisubstitution (Bellamy 1954).

The formation of 4-methoxy-2-methylaminobenzoic acid by the action of methanolic potassium hydroxide on the mononitro derivative of the alkaloid shows this to be 7-methoxy-1-methyl-3-nitro-2-phenyl-4-quinolone ; the dinitro derivative must be 3,6(or 8)-dinitro-7-methoxy-1-methyl-2-phenyl-4-quinolone. Hydrolytic splitting of the nitropyridone ring is closely paralleled by the observation of Kaluza and Perold (1955) that 3-nitrocoumarone is hydrolysed by boiling water to 2-hydroxy-ω-nitrotoluene and formic acid.

By analogy with the nitro derivatives it may be inferred that the bromo derivatives of the alkaloid are the 3-bromo and 3,6(or 8)-dibromo compounds. In the course of synthesizing 4-methoxy-2-methylaminobenzoic acid for comparison with the specimen obtained by degradation of I, the following previously undescribed compounds were prepared : methyl and ethyl 4-methoxy-2-nitrobenzoates, and ethyl 2-amino-4-methoxybenzoate.

III. Experimental

All melting points are corrected unless otherwise stated. Microanalyses were made by the C.S.I.R.O. Microanalytical Laboratory at the University of Melbourne.

(*a*) *Extraction of the Bark and Separation of the Tertiary Bases*

(i) Milled bark (610 g) was exhaustively percolated with methanol, the methanol evaporated under reduced pressure, and the viscous residue shaken with benzene (1000 ml) and aqueous hydrochloric acid (2% ; 1500 ml). Chromatography on neutral alumina of the benzene extract failed to detect the presence of weakly basic substances similar to those described in Section III (*a*) (iii). The aqueous acid solution was basified with sodium bicarbonate, extracted rapidly with chloroform (4 × 500 ml), and immediately reacidified to prevent decomposition of the water-soluble bases. The combined chloroform extracts were evaporated, the residue taken up in benzene (discarding any insoluble material), and filtered through alumina (*c.* 20 g). Evaporation of the filtrate left the combined tertiary bases (5·4 g, 0·9%).

(ii) Partial separation of the crude tertiary base mixture was effected by refluxing with several portions of ether and concentrating the combined ether extracts to give impure lunacrine. Purification by recrystallization first from ether and finally from aqueous methanol gave *lunacrine* as colourless needles, m.p. 96–96·5 °C (air-dried) or 117–118 °C (dried under reduced pressure); $[\alpha]_D^{20}$ (anhydrous) —51° (*c*, 1·77 in ethanol) (Found: C, 70·5; H, 7·2; N, 5·0; CH_3O, 11·2; $CH_3(N)$, 7·6%. Calc. for $C_{16}H_{19}O_3N$: C, 70·3; H, 7·0; N, 5·1; CH_3O, 11·4; $CH_3(N)$, 5·5%). Lunacrine picrate, fine yellow needles from ethanol, melted at 208·5–209·5 °C. Steldt and Chen (1943) report the following constants for lunacrine: m.p.'s 95·5 and 115 °C (anhydrous), $[\alpha]_D^{28}$ —58° in 95% ethanol. Dieterle and Beyl (1937) record m.p. 208 °C for lunacrine picrate.

The ether-insoluble portion of the crude bases was combined with the lunacrine mother liquors and converted, by means of methanolic hydrogen chloride, to the mixed hydrochlorides. After removal of solvent and excess hydrogen chloride these were extracted three times with boiling acetone. The second and third acetone extracts on standing deposited a small amount of crystalline hydrochloride, the base from which separated from ethyl acetate as colourless prisms, $[\alpha]_D^{20}$ —38° (*c*, 2·322 in chloroform), m.p. 222–223·5 °C (Found: C, 66·8; H, 6·1; N, 4·9; CH_3O, nil; $CH_3(N)$, 7·0%. Calc. for $C_{16}H_{17}O_4N$: C, 66·9; H, 5·9; N, 4·9; $CH_3(N)$, 5·2%). Because of the proximity of the m.p. to that of the base, m.p. 219 °C, named by Boorsma (1904) *lunine*, this name is applied to it. The identity of this alkaloid with a base of the same m.p. isolated by Horning and Goodwin from *L. amara* has been established by those workers. Lunine hydrochloride, colourless needles from acetone, has m.p. 215–216 °C (decomp.)* (Found: C, 59·3; H, 5·7; Cl, 11·4%. Calc. for $C_{16}H_{17}O_4N.HCl$: C, 59·3; H, 5·6; Cl, 11·0%). From the acetone-soluble hydrochlorides a further quantity of lunacrine was obtained, while the acetone-insoluble hydrochloride consisted essentially of the hydrochloride of 7-methoxy-1-methyl-2-phenyl-4-quinolone (I), the properties of which are described under Section III(c).

The yields of the three components varied and the following percentages for one separation should be regarded as minimal:

Lunacrine, 0·45; lunine, 0·03; alkaloid I, 0·14.

(iii) The acidified water-soluble base solution after the chloroform-extractable tertiary bases had been removed (Section III (*a*) (i)) was made strongly alkaline with sodium hydroxide; an oily precipitate formed at once. The mixture was heated on the water-bath for an hour, cooled, and extracted with chloroform and the residue (18·4 g) after evaporation of the chloroform extracted with three portions of 2% aqueous hydrochloric acid. From the combined acid solutions was obtained 4·8 g base which was converted to the hydrochloride and crystallized from 15% hydrochloric acid. The product was the hydrochloride of 7-methoxy-1-methyl-2-phenyl-4-quinolone from which the alkaloid (2·2 g, 0·26%) was recovered and identified by m.p. and mixed m.p. The material not soluble in 2% hydrochloric acid is a complex mixture of weakly basic substances; attempts to separate the constituents were unsuccessful. Extraction of the bark in the presence of lime gives rise to a like mixture of weakly basic artefacts.

Milled bark (500 g) and slaked lime (250 g) were mixed with the minimum amount of water, air-dried, and percolated with trichloroethylene. The dark brown gum (30·5 g) remaining after evaporation of the trichloroethylene was stirred with a small volume of ether and crystallized on standing. The filtrate from the crystals deposited further material on long standing. Extraction of a benzene solution of the combined crystalline materials (21·4 g, 4·3%) with 2% aqueous hydrochloric acid gave 7-methoxy-1-methyl-2-phenyl-4-quinolone (2·0 g, 0·4%), identified by m.p. and mixed m.p. The bulk of the alkaloid used in the degradative studies was obtained in this way. No lunine was isolated by this procedure and only a trace of lunacrine could be detected.

(iv) An approximate figure for the total alkaloid content of the bark was obtained as follows. The methanol extract from 56 g bark was evaporated and the concentrate distributed between benzene and aqueous hydrochloric acid as described in Section III (*a*) (i). To the aqueous acid solution was added saturated aqueous picric acid until no further precipitation took place. The

* Boorsma states that his lunine crystallizes, as the free base, from 10% hydrochloric acid. However, he may have been misled by similarity of m.p. between base and hydrochloride.

clear aqueous solution was decanted from the gummy precipitate which was washed with a little water, dried, and weighed. Assuming a mean molecular weight for the precipitated bases of 250–300, the precipitated picrate (4·5 g) represented a base content of 4·2–4·5%.

This value is consistent with the yield of artefacts reported in Section III (*a*) (iii) above.

(b) Paper Chromatography of Alkaloid Extracts

(i) Paper chromatograms of tertiary base fractions were run (ascending) with a 1 : 1 mixture of benzene-light petroleum (b.p. 40–60 °C) as mobile phase on paper impregnated with pH 2·5 sodium citrate buffer and ethylene glycol. A mixture of buffer (1 vol), glycol (1 vol), and methanol (2 vol) was applied to the paper which was hung for ½ hr before use. Approximate R_F values are as follows:

7-Methoxy-1-methyl-2-phenyl-4-quinolone	0·2
Lunine	0·5
Lunacrine	0·5(5)
4-Methoxy-2(3′,4′-methylenedioxyphenyl)quinoline*	0·8
4-Methoxy-2-phenylquinoline*	0·9

Spots were detected by their fluorescence under ultraviolet light.

Using this system, chromatograms were run with extracts of *L. quercifolia* and *L. amara* leaves and bark. To minimize the possibility that the tertiary bases may be artefacts arising during working up, methanol extracts were prepared at room temperature immediately before placing on the papers; the time elapsing from the initial contact of the plant material with the methanol to the commencement of the running of the paper did not exceed 10 min. In each instance clear evidence was obtained of the presence of bases with R_F values the same as those of lunacrine and I, and fluorescing similarly under ultraviolet light.

(ii) The benzene-light petroleum system is inapplicable to the water-soluble bases for which the following was used. Papers were impregnated with 1 : 1 pH 2·2 McElvain buffer : glycol and run (descending) with water-saturated *iso*pentanol as mobile phase. 7-Methoxy-1-methyl-2-phenyl-4-quinolone, lunacrine, and lunine run near the solvent front. The water-soluble bases give rise to five spots in the range R_F 0·2–0·7, all five of which appear in chromatograms of extracts of the bark of *L. quercifolia* and of extracts of two samples of leaves of *L. amara*. All five bases may be present in extracts of *L. quercifolia* leaves but only four show up clearly. Chromatograms of extracts of *L. amara* bark show three strong spots, one weak and one doubtful. Weak spots with R_F values in the range 0·7–0·9 also appear; these have not been identified, but 4-methoxy-2-phenylquinoline and 4-methoxy-2(3′,4′-methylenedioxyphenyl)quinoline have R_F values in this range. The result of a typical chromatogram of an extract of *L. quercifolia* bark is as follows:

R_F Values	Spots	Fluorescence	R_F Values	Spots	Fluorescence
0·9(5)–1·0	strong	light blue	0·6	—	dark blue
0·9	very weak	,, ,,	0·5(5)	—	yellow
0·8(5)	strong	dark blue	0·4	strong	light blue
0·7	very strong	light blue	0·2(5)	—	yellow

(c) Properties of 7-Methoxy-1-methyl-2-phenyl-4-quinolone

(i) The alkaloid crystallized from ethanol as colourless needles, m.p. 199·5–200·5 °C. It was optically inactive (Found: C, 77·1; H, 5·8; N, 5·4; CH_3O, 11·6; CH_3(N), 5·1%; CH_3(C), nil; equiv. wt. (titration with *p*-toluenesulphonic acid in chloroform solution), 270. Calc. for $C_{17}H_{15}O_2N$: C, 77·0; H, 5·7; N, 5·3; CH_3O, 11·7; CH_3(N), 5·7%; **mol. wt.**, 265·3). Ultraviolet absorption, in ethanol solution: $\lambda_{max.}$ 250, 257, 314, and 323 mμ (log ε 4·54, 4·52, 4·14, and 4·15 respectively), $\lambda_{min.}$ 275 mμ (log ε 3·35); in ethanol solution containing 5 equiv. HCl: $\lambda_{max.}$ 251, *256*, 316, and 328 mμ (log ε 4·59, 4·50, 4·06, and 4·10 respectively) $\lambda_{min.}$ 281 mμ (log ε 3·35).

* Kindly provided by Dr. E. C. Horning.

The hydrochloride separated from 5% hydrochloric acid as colourless needles, m.p. 248·5 °C (decomp. uncorr.) (Found : C, 67·3 ; H, 5·3 ; Cl, 11·8%. Calc. for $C_{17}H_{15}O_2N.HCl$: C, 67·7 ; H, 5·3 ; Cl, 11·8%). The picrate, yellow needles from ethanol, melted at 220–220·5 °C (Found : C, 55·9 ; H, 3·6 ; N, 10·9%. Calc. for $C_{17}H_{15}O_2N.C_6H_3O_7N_3$: C, 55·9 ; H, 3·6 ; N, 11·3%).

(ii) The alkaloid gave a bright blue colour with gallic acid/sulphuric acid, but no colour with phloroglucinol/sulphuric acid. It did not react with nitrous acid, ethanolic 2,4-dinitrophenylhydrazine, acetic anhydride in the presence of either pyridine or anhydrous sodium acetate, ethanolic potassium hydroxide (4%), 1 : 1 ethanolic hydrochloric acid (5N), or zinc and hydrochloric acid. It was recovered unchanged after attempted hydrogenation over Raney nickel, palladium-charcoal, or Adams platinum catalysts, and after attempted oxidation by potassium permanganate in acetone, boiling aqueous chromic acid, or selenium dioxide. The alkaloid was also recovered unchanged after the hydrochloride had been heated at 250–270 °C for 5 min.

(iii) No reaction occurred when a solution of the alkaloid in chloroform containing excess methyl iodide was refluxed for 8 hr, but heating with methyl iodide in a sealed tube at 100 °C for 6 hr gave the methiodide, almost colourless plates from water (charcoal) which melted with decomposition at 133·5 °C (uncorr.), resolidified, then remelted at 191–195 °C (Found : C, 50·9 ; H, 4·8%. Calc. for $C_{17}H_{15}O_2N.CH_3I.H_2O$: C, 50·8 ; H, 4·7%).

The methiodide was reconverted to the parent base (m.p. and mixed m.p.) by heating at 140 °C for 10 min or by the action of 2½% aqueous sodium hydroxide at room temperature.

(iv) 7-Hydroxy-1-methyl-2-phenyl-4-quinolone, prepared by refluxing a solution of the alkaloid in 1 : 1 HBr (46%)/CH_3COOH for 8 hr, separated from methanol as colourless prisms, m.p. 344–346 °C. It was also obtained by heating the alkaloid for 2 hr at 200 °C with a 5% solution of potassium hydroxide in ethylene glycol (Found : C, 76·3 ; H, 5·1 ; N, 5·9%. Calc. for $C_{16}H_{13}O_2N$: C, 76·5 ; H, 5·2 ; N, 5·6%). Methylation with excess dimethyl sulphate and sodium hydroxide regenerated the alkaloid (m.p. and mixed m.p. 199–200 °C). Acetylation with acetic anhydride/pyridine gave 7-acetoxy-1-methyl-2-phenyl-4-quinolone, colourless needles from benzene, m.p. 158–158·5 °C (Found : C, 74·1 ; H, 5·5%. Calc. for $C_{18}H_{15}O_3N$: C, 73·7 ; H, 5·1%).

7-Hydroxy-1-methyl-2-phenyl-4-quinolone (1 g) was oxidized by adding slowly to warm 68% nitric acid. When the initial reaction ceased, the mixture was refluxed for ½ hr, and the nitric acid evaporated under reduced pressure. The residue was triturated with water, and the solid filtered off and recrystallized by solution in a little 68% nitric acid and dilution with water. The resulting cream prisms decomposed with evolution of gas at c. 170 °C, resolidified and remelted at 218–219 °C (Found : C, 58·3 ; H, 4·5%. Calc. for $C_{14}H_{11}O_5N.H_2O$: C, 57·7 ; H, 4·5%). Decarboxylation by boiling an acetic acid solution gave 1-methyl-6-phenyl-4-pyridone-3-carboxylic acid, colourless needles from ethanol, m.p. 219–220 °C (Found : C, 68·4 ; H, 4·7 ; N, 6·4 ; CH_3(N), 6·2%. Calc. for $C_{13}H_{11}O_3N$: C, 68·1 ; H, 4·8 ; N, 6·1 ; CH_3(N), 6·6%).

(v) Bromination of the alkaloid in acetic acid solution by gradual addition of bromine (5% in acetic acid) gave a mixture of bromo compounds which could not be separated chromatographically on alumina. Elution with chloroform from a silica gel column, however, gave a monobromo derivative, colourless needles from ethanol, m.p. 230·5–231·5 °C (uncorr.) (Found : C, 59·7 ; H, 4·3%. Calc. for $C_{17}H_{14}O_2NBr$: C, 59·3 ; H, 4·1%) and a dibromo derivative, colourless leaflets from chloroform/ethanol, m.p. 305–306 °C (Found : C, 48·5 ; H, 3·3%. Calc. for $C_{17}H_{13}O_2NBr_2$: C, 48·2 ; H, 3·1%).

(*d*) *Action of Nitric Acid on the Alkaloid*

(i) The alkaloid (10 g) was added slowly to 68% nitric acid (45 ml), the mixture warmed gently until reaction commenced, and finally refluxed for an hour. The reaction mixture was poured into water and the solution extracted repeatedly with chloroform. The chloroform extracts were washed with water, the washings combined with the aqueous nitric acid solution, and evaporated under reduced pressure to c. 50 ml. On standing, pale yellow crystals (3·61 g) separated from the nitric acid. Several recrystallizations from 68% nitric acid gave almost colourless plates, m.p. 178–179 °C (decomp.) (Found : C, 27·6 ; H, 1·8 ; N, 23·2%. Calc. for $C_7H_5O_6N_5$: C, 27·7 ; H, 1·7 ; N, 23·1%). A synthetic specimen of 3-hydroxy-2,4,6-

trinitrophenyl methyl nitramine prepared by the action of boiling 68% nitric acid on *NN*-dimethyl-*m*-phenetidine (b.p. 248–250 °C/760 mm ; Reverdin (1915) reports b.p. 256 °C) was obtained as colourless plates from nitric acid, m.p. 177–179 °C (decomp.) (Found : C, 27·7 ; H, 1·7 ; N, 22·9%). A mixture with the alkaloid degradation product had m.p. 177–179 °C (decom.p.). An additional 1·45 g of crude 3-hydroxy-2,4,6-trinitrophenyl methyl nitramine was obtained in the course of working up the chloroform extracts.

The combined chloroform extracts, after washing three times with 2% sodium hydroxide and once with water, were evaporated and the residue (4·06 g) crystallized first from chloroform, then three times from methyl *n*-propyl ketone. The dinitro derivative of the alkaloid, 3,6(or 8)-dinitro-7-methoxy-1-methyl-2-phenyl-4-quinolone, separated as pale yellow prisms, m.p. 308·5–309·5 °C (uncorr.) (Found : C, 57·8 ; H, 4·1 ; N, 11·8%.* Calc. for $C_{17}H_{13}O_6N_3$: C, 57·5 ; H, 3·7 ; N, 11·8 ; CH_3O, 8·7 ; CH_3(N), 4·2%).

The sodium hydroxide washings of the chloroform extract were acidified with nitric acid and extracted three times with chloroform, the extracts on evaporation leaving a 1·96 g semi-crystalline residue. Crystallization with water (charcoal) gave benzoic acid, m.p. and mixed m.p. with an authentic specimen, 120–122 °C (Found : C, 68·7 ; H, 5·1%. Calc. for $C_7H_6O_2$: C, 68·9 ; H, 4·9%).

(ii) When a solution of the alkaloid in 68% nitric acid was refluxed for 10 min and worked up as described above, the dinitro derivative $C_{17}H_{12}O_6N_2$ was not obtained. In its place was isolated a mononitro derivative, 7-methoxy-1-methyl-3-nitro-2-phenyl-4-quinolone, pale yellow needles from acetic anhydride, m.p. 309–310 °C. Mixed with the dinitro derivative, the m.p. was depressed below 280 °C (Found : C, 66·0 ; H, 4·6 ; O, 20·4 ; N, 9·4 ; CH_3O, 10·1 ; CH_3(N), 4·7%. Calc. for $C_{17}H_{14}O_4N_2$: C, 65·8 ; H, 4·5 ; O, 20·6 ; N, 9·0 ; CH_3O, 10·0 ; CH_3(N), 4·8%).

Refluxing with 68% nitric acid for an hour converted the mononitro to the dinitro derivative, the m.p. of the product being depressed below 280 °C on admixture with the starting material. The dinitro derivative dissolves immediately to a yellow solution on gentle warming with N/1 ethanolic potash, and is recovered unchanged (m.p. and mixed m.p.) on acidification. The mononitro derivative does not behave in this way.

(e) Action of Alcoholic Potassium Hydroxide on the Nitro Derivatives of the Alkaloid

(i) Reaction of the mononitro compound $C_{17}H_{14}O_4N_2$ with ethanolic potassium hydroxide : The mononitro compound (2·6 g) was refluxed with ethanolic potassium hydroxide (10% ; 100 ml) for 1½ hr, solid separating slowly from the deep yellow reaction mixture. Water (50 ml) was added and all the ethanol removed. The orange potassium salt which separated on standing was filtered off, dissolved in water, and the solution saturated with carbon dioxide. The precipitate (1·05 g) was three times crystallized from carbon tetrachloride and twice from benzene-light petroleum, 4-methoxy-2-methylamino-ω-nitroacetophenone being obtained as yellow needles, m.p. 149·5–150·5 °C (Found : C, 53·6 ; H, 5·5 ; N, 12·8 ; CH_3O, 13·2%. Calc. for $C_{10}H_{12}O_4N_2$: C, 53·6 ; H, 5·4 ; N, 12·5 ; CH_3O, 13·8%). The filtrate from the potassium salt was acidified with hydrochloric acid and extracted with chloroform. The residue (1·3 g) after evaporation of the chloroform was extracted with ether, the ether-soluble portion sublimed and crystallized from water giving benzoic acid, m.p. and mixed m.p. 121–122 °C.

(ii) Reaction of the dinitro compound $C_{17}H_{12}O_6N_2$ with ethanolic potassium hydroxide : The dinitro compound (1·0 g) was refluxed with ethanolic potassium hydroxide (10% ; 100 ml) for 1 hr, during which a solid separated from the reaction mixture. After concentration to 50 ml the solid was filtered off, dissolved in water, and the solution acidified with hydrochloric acid. Fractional crystallization of the precipitate from ethanol gave two crops, the first (0·42 g), after

* Dr. K. W. Zimmermann of the C.S.I.R.O. Microanalytical Laboratory reports that the substance behaved abnormally in the methoxyl determination, evolving methyl iodide very slowly. For that reason methoxyl and methylimino were determined together (Found : CH_3O+CH_3N as CH_3, 8·4%). The methoxyl content found after prolonged distillation was 8·2%.

several recrystallizations from ethanol gave ω-5(or 3)-dinitro-4-ethoxy-2-methylaminoacetophenone as yellow needles, m.p. 198–199 °C (Found : C, 46·7 ; H, 4·8 ; N, 14·6%. Calc. for $C_{11}H_{13}O_6N_3$: C, 46·6 ; H, 4·6 ; N, 14·8%). The second fraction (0·2 g) was recrystallized from chloroform and finally aqueous ethanol giving yellow needles of 4-ethoxy-2-methylamino-5(or 3)-nitrobenzoic acid, m.p. 248–249 °C (decomp.) (Found : C, 50·2 ; H, 5·0%. Calc. for $C_{10}H_{12}O_5N_2$: C, 50·0 ; H, 5·0%).

The filtrate from the mixed potassium salts was diluted with water, the ethanol evaporated, the solution acidified with hydrochloric acid and extracted with ether. The residue (0·4 g) after evaporation of the ether gave, after extraction with hot water (charcoal), sublimation, and crystallization from water, benzoic acid, m.p. and mixed m.p. 121–122 °C.

(iii) Reaction of the mononitro compound with methanolic potassium hydroxide was very much slower than with ethanolic potassium hydroxide. The reaction was therefore carried out by heating the mononitro compound (0·57 g) with methanolic potassium hydroxide (10% ; 20 ml) in a sealed tube at 105 °C for 8 hr. The methanol was removed, replaced by water, and the products separated into a non-acidic fraction (0·03 g), a fraction (0·24 g) soluble in sodium bicarbonate solution, and a fraction (0·22 g) insoluble in sodium bicarbonate solution but soluble in sodium carbonate solution. The sodium bicarbonate-soluble material was identified, after recrystallization, as benzoic acid (m.p. and mixed m.p.) ; the sodium carbonate-soluble material was crystallized from benzene-light petroleum and finally several times from aqueous ethanol. It was obtained as colourless needles, m.p. 164–165 °C (decomp.) (Found : C, 59·8 ; H, 6·2%. Calc. for $C_9H_{11}O_3N$: C, 59·7 ; H, 6·1%). Authentic 4-methoxy-2-methylaminobenzoic acid, prepared from methyl 2-amino-4-methoxybenzoate (see Section III (*f*)) melted at 164–165 °C (decomp.) ; a mixture of the two specimens behaved likewise. Heilbron *et al.* (1925) report m.p. 165 °C.

(iv) The dinitro compound (1·0 g) was refluxed for 1 hr with methanolic potassium hydroxide (10% ; 100 ml) and the mixture concentrated to 50 ml. The resulting yellow solid was filtered off, dissolved in water, and the solution acidified with hydrochloric acid, giving a yellow crystalline precipitate (0·4 g). Recrystallization from aqueous methanol (three times) and from methanol (once) gave 4-methoxy-2-methylamino-5(or 3)-nitrobenzoic acid, bright yellow needles, m.p. 265·5 °C (decomp.) (Found : C, 47·9 ; H, 4·4 ; N, 12·4%. Calc. for $C_9H_{10}O_5N_2$: C, 47·8 ; H, 4·4 ; N, 12·4%).

(*f*) *1-Methyl-2-phenyl-4-quinolone*

Condensation of acetophenone diethyl ketal with methyl anthranilate as described by Fuson and Burness (1946) gave 2-phenyl-4-quinolone, m.p. 252–253 °C (uncorr.). Methylation of the quinolone with dimethyl sulphate and sodium hydroxide gave 1-methyl-2-phenyl-4-quinolone, colourless needles from aqueous methanol, m.p. 143–144 °C after vacuum drying at 80 °C (cf. Goodwin, Smith, and Horning 1957) (Found : C, 81·8 ; H, 5·6 ; N, 5·9%. Calc. for $C_{16}H_{13}ON$: C, 81·7 ; H, 5·5 ; N, 6·0%). Ultraviolet absorption in ethanol solution : $\lambda_{max.}$ 249, 324, and 335 mμ (log ε 4·51, 4·11, and 4·17 respectively), $\lambda_{min.}$ 278 mμ (log ε 3·43).

Attempted synthesis of 2-phenyl-7-methoxy-4-quinolone by condensation of acetophenone diethyl ketal with ethyl 2-amino-4-methoxybenzoate was unsuccessful ; no quinolone could be recovered from the reaction mixture. The *ethyl 2-amino-4-methoxybenzoate*, prepared by reduction of the nitro ester with hydrogen over Raney nickel at 100 °C/1600 lb/in², separated from light petroleum as colourless needles, m.p. 68·5–69·5 °C (Found : C, 61·5 ; H, 6·7 ; N, 7·3%. Calc. for $C_{16}H_{13}O_3N$: C, 61·5 ; H, 6·7 ; N, 7·2%). *Ethyl 4-methoxy-2-nitrobenzoate* was obtained as colourless needles from light petroleum, m.p. 72–72·5 °C (Found : C, 53·7 ; H, 4·9 ; N, 6·3%. Calc. for $C_{10}H_{11}O_5N$: C, 53·5 ; H, 4·9 ; N, 6·2%). *Methyl 4-methoxy-2-nitrobenzoate*, colourless needles from light petroleum, m.p. 68–68·5 °C (Found : C, 51·6 ; H, 4·5%. Calc. for $C_9H_9O_5N$: C, 51·2 ; H, 4·3%). Methyl 2-amino-4-methoxybenzoate, prepared by reduction of the nitro ester, and crystallized first from light petroleum and finally from aqueous methanol, had m.p. 78–79 °C. Friedlander, Bruckner, and Deutsch (1912) report m.p. 75 °C. Rodionov and Fedorova (1939) report m.p. 116–118 °C but the identity of their substance is open to doubt ; it could have been the methyl ester of 2-amino-5-methoxybenzoic acid.

(g) Synthesis of 7-Methoxy-1-methyl-2-phenyl-4-quinolone

7-Methoxy-2-phenyl-4-quinolone was prepared by the method of Elderfield *et al.* (1946) from benz-*m*-anisidide (m.p. 111–112 °C) by way of the chloroimide (b.p. 160–165 °C/2 mm) and 3-carbethoxy-7-methoxy-2-phenyl-4-quinolone (m.p. 241–241·5 °C; Elderfield *et al.* (1946) report m.p. 232–233 °C). Saponification and decarboxylation gave 7-methoxy-2-phenyl-4-quinolone, m.p. 290–291 °C (uncorr.), after crystallization from 40% aqueous acetic acid (Found : C, 76·6; H, 5·2; CH_3O, 12·0%. Calc. for $C_{16}H_{13}O_2N$: C, 76·5; H, 5·2; CH_3O, 12·3%). Elderfield *et al.* (1946) report m.p. 282–283 °C. Methylation of the quinolone with 10% aqueous sodium hydroxide and excess dimethyl sulphate gave 7-methoxy-1-methyl-2-phenyl-4-quinolone, colourless needles from methanol, m.p. 199·5–200·5 °C, alone or mixed with the natural alkaloid (Found : C, 77·1; H, 5·7; N, 5·4; CH_3O, 11·8; $CH_3(N)$, 5·4%. Calc. for $C_{17}H_{15}O_2N$: C, 77·0; H, 5·7; N, 5·3; CH_3O, 11·7; $CH_3(N)$, 5·7%). Ultraviolet absorption, in ethanol solution : $\lambda_{max.}$ 248, 257, 316, and 323 mμ (log ε 4·55, 4·53, 4·15, and 4·15 respectively), $\lambda_{min.}$ 275 mμ (log ε 3·47). The infra-red (" Nujol mull ") spectrum of the synthetic compound was identical with that of the natural base. The hydrochloride formed colourless needles, m.p. 248 °C (decomp.), alone or mixed with the alkaloid hydrochloride. The picrate, yellow needles from ethanol, melted at 220–220·5 °C, alone or mixed with the alkaloid picrate (Found : C, 56·0; H, 3·7%. Calc. for $C_{17}H_{15}O_2N.C_6H_3O_7N_3$: C, 55·9; H, 3·6%). Demethylation by refluxing for 8 hr with 1 : 1 HBr (46%)/CH_3COOH gave 7-hydroxy-1-methyl-2-phenyl-4-quinolone, m.p. and mixed m.p. with a specimen prepared from the alkaloid, 344–346 °C (uncorr.).

(h) Synthesis of 7-Methoxy-1-methyl-3-phenyl-4-quinolone

Following the procedure of Adams and Hey (1950), β-(*m*-anisidino)-α-phenylacrylic ester prepared from *m*-anisidine and ethyl formyl phenyl acetate was cyclized by boiling a solution in diphenyl ether for 1½ hr. 7-Methoxy-3-phenyl-4-quinolone, which separated on cooling (yield, 74%), crystallized from pyridine as colourless needles, m.p. 303–304 °C (Found : C, 76·5; H, 5·3; N, 5·6%. Calc. for $C_{16}H_{13}O_2N$: C, 76·5; H, 5·2; N, 5·6%). The quinolone is sparingly soluble in cold 5% aqueous sodium hydroxide but dissolves on warming. Methylation with excess dimethyl sulphate and sodium hydroxide gave 7-methoxy-1-methyl-3-phenyl-4-quinolone, colourless needles from methanol, m.p. 195–195·5 °C (Found : C, 77·1; H, 5·8; N, 5·2; CH_3O, 11·3; $CH_3(N)$, 5·2%. Calc. for $C_{17}H_{15}O_2N$: C, 77·0; H, 5·7; N, 5·3; CH_3O, 11·7; $CH_3(N)$, 5·7%). A mixture with 7-methoxy-1-methyl-2-phenyl-4-quinolone melted at *c.* 160 °C. Ultraviolet absorption, in ethanol solution : $\lambda_{max.}$ 237, 270, *307*, and 331 mμ (log ε 4·39, 4·50, 3·86, and 4·03 respectively), $\lambda_{min.}$ 295 mμ (log ε 3·79).

Demethylation by refluxing for 7 hr with 1 : 1 HBr (46%)/CH_3COOH gave 7-hydroxy-1-methyl-3-phenyl-4-quinolone, colourless needles from 50% aqueous acetic acid, m.p. 299·5–300·5 °C (Found : C, 76·3; H, 5·2%. Calc. for $C_{16}H_{13}O_2N$: C, 76·5; H, 5·2%). The substance is readily soluble in cold 5% aqueous sodium hydroxide.

(i) Spectroscopic Data

Infra-red spectra were measured on a Perkin-Elmer Model 21 double-beam instrument (R.N.H.) or a Perkin-Elmer Model 12C converted to double-pass operation (J.B.W.). Ultraviolet spectra were measured with a Hilger Uvispek Spectrophotometer.

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CHEMISTRY OF NON-ENZYMIC BROWNING

IV. DETERMINATION OF AMINO ACIDS AND AMINO ACID-DEOXYFRUCTOSES IN BROWNED FREEZE-DRIED APRICOTS

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Summary

1-(*N*-Amino acid)-1-deoxyfructoses have been determined by elution chromatography on columns of a buffered cation exchange resin following the method described by Moore and Stein (1954*a*) for the determination of amino acids. This method has been used to determine the free amino acids and ammonia in freeze-dried apricots before and after storage for 12 months at 25 °C and 70 per cent. R.H., as well as to determine the 1-(*N*-amino acid)-1-deoxyfructoses and related compounds formed (Anet and Reynolds 1957) during storage. The total free amino acid decreased by 61 per cent. and the ammonia by 9 per cent., the changes in individual amino acids ranging from 22 to 81 per cent. The amino acid-deoxyfructoses and related compounds accounted for 90 per cent. of the free amino acid lost, the actual discrepancy being 1·2 mM/100 g dry weight of fruit.

I. INTRODUCTION

In Part I of this series (Anet and Reynolds 1957), it was shown that browned freeze-dried apricot purée which had been stored at 25 °C and 70 per cent. R.H. contained 1-(*N*-amino acid)-1-deoxyfructoses and related compounds formed from the reaction of glucose with amino acids and ammonia. Analysis of the fractions obtained by displacement chromatography on columns of a cation-exchange resin showed that the total amino acid lost was approximately equal, on a molar basis, to the amino acid-deoxyfructoses (and related compounds) formed. The individual amino acids, and ammonia, have now been determined before and after storage by elution chromatography on columns of a buffered cation-exchange resin (Moore and Stein 1954*a*) and it has been found that the reaction products in the browned purée can be determined by the same method.

The chromatographic method described by Moore and Stein (1954*a*) was followed. The resolution of proline and glutamic acid proved difficult but separation was regularly achieved with "Zeo Karb 225–4NC" if the column temperature was not raised from 30 to 50 °C until after the emergence of alanine. The amino acids emerged from the column in the expected order but the elution volumes (Fig. 1) were appreciably lower than those recorded by Moore and Stein (1954*a*). The same method was used to determine the elution volumes (Fig. 1) of the synthetic 1-(*N*-amino acid)-1-deoxysugars previously described (Anet 1957; Anet and Reynolds 1957). These compounds gave the same ninhydrin

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colour value per mole as the parent amino acid. Asparaginodeoxyfructose could not be separated from deoxythreonino- and deoxyserinofructose even in equimolar mixtures and deoxyvalinofructose emerged with alaninodeoxyfructose. Ammonia was determined on a 15 cm column of " Zeo Karb 225–4NC " run at 50 °C with 0·4N citrate buffer, pH 5·26 (Moore, personal communication).

The samples used were freeze-dried apricot purée stored for 12 months at 25 °C and 70 per cent. R.H. and for 24 months at −20 °C and 3·8 per cent. water content. Storage at a low temperature with low water content reduces the reaction rate to such a low level that this latter sample was accepted as equivalent to the freshly prepared material. It was equilibrated to 70 per cent. R.H.

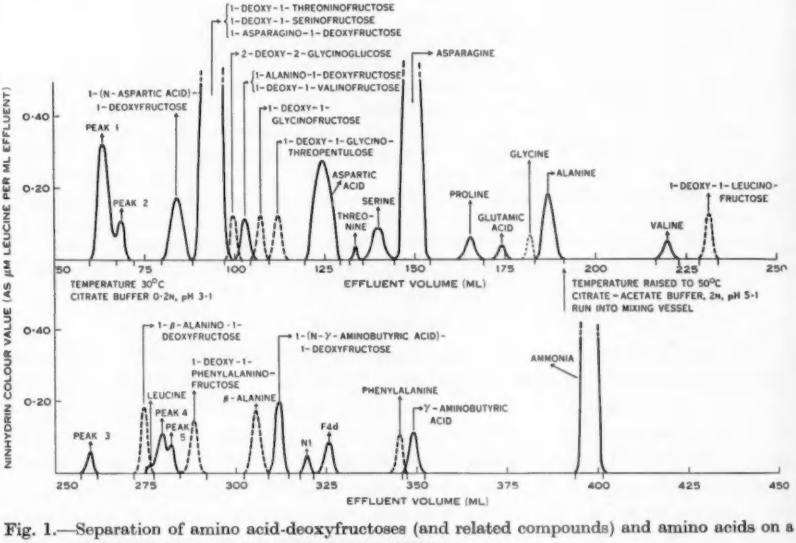

Fig. 1.—Separation of amino acid-deoxyfructoses (and related compounds) and amino acids on a column (150 by 0·9 cm) of " Zeo Karb 225–4NC ".

—— Peaks given by freeze-dried apricot purée stored 12 months at 25 °C and 7 per cent. R.H.

---- Peaks given by compounds not found in this sample of browned fruit.

immediately before extraction to avoid corrections for water content. Buffered (pH 2·2) aqueous extracts were prepared from these samples and applied to the column of buffered cation-exchange resin. The amino acids were identified by their order of emergence, their elution volume, and their behaviour on paper chromatograms. Ten of the amino acids previously detected in apricots (Reynolds 1957) and freeze-dried apricots (Anet and Reynolds 1957) were determined in both samples (Table 1) and a trace of glycine was detected. The concentration of the other amino acids present was too low to permit their detection by this method. The total free amino acid lost during storage was 61 per cent., but the loss of individual acids varied from 22 per cent. for proline to 81 per cent. for glutamic acid (Table 1).

TABLE 1

CATIONIC CONSTITUENTS OF FREEZE-DRIED APRICOT PURÉE BEFORE AND AFTER STORAGE FOR 12 MONTHS AT 25 °C AND 70 PER CENT. RELATIVE HUMIDITY

Constituents	Before Storage			After Storage			
	No. of Values	Mean (mM/100 g dry wt. of fruit)	Standard Error*	No. of Values	Mean (mM/100 g dry wt. of fruit)	Standard Error*	Free Amino Acid Lost (%)
Peak 1 (F1*a*)		—		3	0·55	0·101	
Peak 2		—		3	0·21	0·057	
(*N* - Aspartic acid) - deoxyfructose		—		4	0·63	0·071	
Deoxythreoninofructose, Deoxyserinofructose, Asparaginodeoxyfructose		—		6	3·95	0·185	
Alaninodeoxyfructose, Deoxyvalinofructose		—		8	0·28	0·036	
Aspartic acid	12	0·74	0·028	9	0·61	0·041	††
Threonine	10	0·07	0·026	5	0·04	0·012	
Serine	3	0·49	0·018	9	0·15	0·032	69
Asparagine	3	8·98	0·219	10	2·39	0·112	73
Proline	8	0·73	0·092	8	0·57	0·146	22
Glutamic acid	7	0·26	0·031	4	0·05	0·019	81
Glycine		Trace			Trace		
Alanine	9	0·76	0·018	6	0·53	0·043	30
Valine	8	0·16	0·021		0·04	0·025	75
Peak 3				4	0·19	0·033	
Leucine	6	0·08	0·029		Trace		
Peaks 4 and 5		—		5	0·25	0·040	
(*N*-γ-Aminobutyric acid)-deoxyfructose		—		4	0·38	0·022	
N1 (ammonia derivative)		—		4	0·15	0·047	
F4*d* (asparagine derivative)		—		5	0·20	0·032	
γ-Aminobutyric acid	10	0·46	0·017	4	0·15	0·033	67
Ammonia	3	4·16	0·215	3	4·23	0·179	9‡
Total cationic constituents excluding proline and glutamic acid§		15·90‖			14·93‖		

* Standard error of a single observation.

† Not calculable from these experiments because asparagine and asparaginofructose partially hydrolysed.

‡ Assuming 0·5 mM ammonia formed by hydrolysis of asparagine and its derivatives (calculated from aspartic acid and aspartic acid-deoxyfructose values).

§ Proline and glutamic acid excluded because deoxyprolinofructose would not be estimated and glutamic acid-deoxyfructose would decompose on the column (cf. Anet and Reynolds 1957).

‖ Approximate L.S.D. between these values for $P=0{\cdot}01$ is 0·75 mM/100 g dry weight of fruit.

The browned fruit gave four peaks which were shown to correspond with 1-(*N*-amino acid)-1-deoxyfructoses (Fig. 1). Other peaks were identified as N1, the main product of the glucose-ammonia reaction, and F1*a* and F4*d*, by-products from the reaction between glucose and aspartic acid (F1*a*), or asparagine (F1*a* and F4*d*) (code numbers taken from Anet and Reynolds 1957). Other by-products of these last reactions would be expected, from their behaviour on displacement columns, to be included in the asparaginodeoxyfructose peak. The detection of deoxyprolinofructose was not attempted since the values given in Table 1 would not be affected by this compound. Glutamic acid-deoxyfructose was shown to decompose on displacement columns (Anet and Reynolds 1957) and has not been investigated. Deoxyleucinofructose was not definitely identified. The four unknown peaks (peaks 2–5) did not correspond with any of the amino acid-sugar reaction products so far studied.

Quantitatively the reaction products accounted for 90 per cent. of the free amino acid lost during storage, the actual discrepancy being 1·2 mM/100 g dry weight of fruit (Table 1). This calculation excludes proline and glutamic acid but includes peaks 2–5. In a similar sample stored for 16 months 11 mM of glucose and 8 mM of fructose/100 g dry weight of fruit could not be accounted for (Anet and Reynolds 1957).

II. Experimental

(*a*) *Samples Used.*—Freeze-dried apricot purée (moisture content 3·8%) was prepared as previously described (Anet and Reynolds 1957) and stored at —20 °C. A sample was equilibrated to 70% R.H. over saturated aqueous strontium chloride at 25 °C under reduced pressure and then stored at 25 °C for 12 months, when it was mid-brown in colour. Some freeze-dried purée was taken from —20 °C after 24 months' storage and brought to 70% R.H. along with the sample of browned purée. The moisture content of both samples was 20·6%.

(*b*) *Preparation of Extracts.*—Equilibrated freeze-dried purée (browned or unbrowned) (5·00 g) was mixed with 0·2N sodium citrate buffer pH 2·2 (Moore and Stein 1954*a*) (50 ml) in a water-cooled Waring microblendor for 2 min. The mixture was centrifuged at 8000 r.p.m. for 30 min and the clear supernatant liquor was decanted and stored at —20 °C. Aliquots of 1 or 2 ml were applied to ion-exchange columns for elution chromatography.

(*c*) *Elution Chromatography.*—(i) *Amino Acids in Freeze-Dried Apricot Purée before Browning.* The amino acids were separated on columns (150 by 0·9 cm) of a buffered cation-exchange resin by a combination of normal and gradient elution according to the method of Moore and Stein (1954*a*) with the following modifications: (1) the columns were not packed under pressure as this seriously reduced the flow rate, (2) the column temperature was not increased from 30 to 50 °C until after the emergence of alanine. The effluent from the column was collected in 1 ml fractions until alanine emerged and then in 2 ml fractions. The amino acid content of each fraction was determined by the photometric ninhydrin method of Moore and Stein (1954*b*).

The ion-exchange resins used were (1) "Dowex 50-X4", purchased as 50–100 mesh, bead form, and ground in water in a ball mill until it passed through a 200 mesh sieve, (2) "Zeo Karb 225-10NC", purchased as 20–40 mesh, bead form, and ground dry in a disk grinder until it passed through a 200 mesh sieve, and (3) "Zeo Karb 225-4NC" 200–400 mesh, bead form. Except in the case of serine and asparagine, all three resins were used in obtaining the results shown in Table 1. The separation of serine and asparagine was satisfactory only on columns of resin 3 although a balanced mixture of the authentic acids was separated on the other resins. Resin 3 also gave sharper peaks for some of the other amino acids. Proline and glutamic acid were not

always separated on resins 1 and 2 and could regularly be separated on resin 3 only if the increase in column temperature from 30 to 50 °C was delayed until after the emergence of alanine (cf. Fig. 1). The elution volumes of the amino acids (Fig. 1) were similar for the three resins. The only compounds detected were the amino acids shown in Table 1 and ammonia.

(ii) *Amino Acids and Amino Acid-Deoxyfructoses in Browned Freeze-Dried Apricot Purée.* These compounds were separated and determined by the method described above. " Zeo Karb 225-4NC " was used for all analyses. The peaks found are shown in Figure 1 and the quantitative values in Table 1. Asparaginodeoxyfructose, deoxythreoninofructose, and deoxyserinofructose could not be separated even when the synthetic compounds were run as a balanced mixture and similarly alaninodeoxyfructose and deoxyvalinofructose always emerged together.

(iii) *Amino Acids and Amino Acid Derivatives.* The elution volumes of 1-deoxy-1-glycino-*threo*pentulose and 2-deoxy-2-glycinoglucose (Anet 1957) and of a number of amino acids and amino acid-deoxyfructoses not found in the elution chromatograms of the fruit were determined by the same method. These are shown (see broken-line peaks) in Figure 1.

(iv) *Ammonia in Freeze-Dried Apricot Purées before and after Browning.* Ammonia emerged as a well-defined peak (Fig. 1) in the experiments described above but it was difficult to establish the base line. Ammonia was determined more conveniently and accurately on a 15 by 0·9 cm column of " Zeo Karb 225-4NC ". The column was run at 50 °C and the ammonia was eluted with 0·4N citrate buffer, pH 5·26 (Moore, personal communication). The effluent was collected in 2 ml fractions and the ammonia was determined with ninhydrin (Moore and Stein 1954*b*). The results are shown in Table 1.

(*d*) *Ninhydrin Determinations.*—The ninhydrin colour yields obtained for the amino acids and ammonia (on a molar basis relative to leucine) were the same as those reported by Moore and Stein (1954*b*). The leucine equivalent (cf. Fig. 1) was corrected to give the results shown in Table 1. The same method (Moore and Stein 1954*b*) was used to determine the 1-(*N*-amino acid)-1-deoxyfructoses, 2-deoxy-2-glycinoglucose, and 1-deoxy-1-glycino*threo*pentulose. The colour yield in all cases was the same, on a molar basis, as that given by the parent amino acid and was used to correct the values shown in Table 1. The values for peaks 1–5, N1, and F4*d* (Table 1) are given in leucine equivalents since the peaks were not identified (peaks 2–5) or else the reaction product used for identification was only available as a component of a mixture.

(*e*) *Identification of Elution Peaks.*—The peaks given by the amino acids were identified by (i) the order of elution and the elution volume in comparison with the results obtained for authentic amino acids, (ii) the increase in a peak resulting from the addition of an authentic amino acid to the fruit extract, and (iii) by paper chromatography as follows : half of each effluent fraction was pipetted out and the ninhydrin colour value determined to locate the peaks ; the fractions containing a single amino acid were combined and a suitable aliquot was run through a column of " Zeo Karb 225-10NC " or " Dowex 50-X4 " (5 g, H form) ; the column was washed with water and the amino acid was displaced with a slight excess of 0·5N ammonia ; the amino acid solution was evaporated to a small volume under reduced pressure and run on paper chromatograms by the method previously described (Reynolds 1957).

The reaction products in the browned fruit were identified by the same methods with the aid of the compounds previously synthesized (Anet and Reynolds 1957) or, in the case of F4*d* and N1, appropriate fractions from displacement chromatograms of the cationic constituents of browned fruit (Anet and Reynolds 1957). De-ionized effluent fractions were heated with 0·1N acetic acid (Anet and Reynolds 1957) and the parent amino acid was identified by paper chromatography. Peaks 1 and 2, when combined, de-ionized, and hydrolysed, gave aspartic acid. Peak 1 was augmented by the addition of a by-product (called F1*a* by Anet and Reynolds 1957) from the reaction of aspartic acid (or asparagine) with glucose, with peak 2 appearing as a shoulder. Peaks 3–5 did not correspond with any available synthetic or naturally occurring reaction products. When de-ionized and hydrolysed they gave a weak spot on paper chromatograms in the aspartic acid position. This spot could not be distinguished from a faint spot given by an ineradicable impurity which was present in all available samples of ammonia and ammonium salts. The identity of the peaks given by the browned fruit is shown in Figure 1.

III. Acknowledgments

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SOLUBLE WOOL PROTEINS

I. LIGHT SCATTERING AND VISCOSITY IN AQUEOUS SOLUTIONS

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Summary

S-Carboxymethylkerateine 2 (SCMK2) and α-keratose, two proteins derived from wool, have been characterized by nitrogen content, ultraviolet absorption, refractive index increment, light scattering, and intrinsic viscosity. Variations in the physical properties of different batches are attributed to different degrees of aggregation during the preparation.

The relative viscosity decreased with time and was generally accompanied by an increase in turbidity, indicating aggregation. The effect of heating was to accelerate the fall in viscosity and increase in turbidity. Light scattering investigations showed that dissociation occurred on dilution and in some cases this could be detected by viscosity measurements. The molecular weight of several millions for SCMK2 at pH 6·7 was reduced to less than 1 million by removal of large aggregates by high-speed centrifuging, with an increase in both dissymmetry and intrinsic viscosity. In alkaline buffers at pH 10·5 the proteins were further dissociated and gave molecular weights of the order of 450,000. The behaviour of α-keratose was similar to that of SCMK2.

Measurements on SCMK2 carried out in the presence of sodium dodecyl sulphate gave a molecular weight of 142,000 for the detergent-protein complex, corresponding to 95,000 for the protein, the dissymmetry was near unity and the intrinsic viscosity $0{\cdot}11_5$ dl/g. In 10M acetic acid, 8M urea, and 6M guanidine hydrochloride the apparent molecular weights were 95,000, 140,000, and 210,000 respectively, but these values are only upper limits because of possible selective solvation of the solvent component in such three-component systems.

I. INTRODUCTION

Recent investigations in this laboratory have dealt with the viscosity, sedimentation, and diffusion of two soluble wool keratin derivatives (O'Donnell and Woods 1956*a*, 1956*b*, 1956*c*). One of these was prepared by reduction of the cystine residues and alkylation of the —SH groups so formed (Gillespie 1956), the other by oxidation of the —S—S— bonds to two $-SO_3H$ groups (Alexander, Hudson, and Fox 1950). These investigations clearly indicated the polydispersity of these preparations and suggested that in aqueous solutions aggregation played a major role in their physicochemical properties. The effects of time, pH, and ionic strength were explained by variations in the state of aggregation of the protein. Disaggregation could be effected in 8M urea, or by forming a complex with sodium dodecyl sulphate. The present investigation was undertaken to obtain more information on the polydispersity especially at low protein concentrations using the techniques of light scattering and viscosity.

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II. Experimental

(a) *Materials*

(i) *Wool Protein Derivatives.*—The *S*-carboxymethylkerateine 2 (SCMK2) was prepared from Merino 64's wool by reducing with alkaline thioglycollate and coupling the —SH groups with iodoacetate according to the method of Gillespie (1956). Several different preparations of SCMK2 were used. Electrophoresis in 0·1 ionic strength glycine-sodium hydroxide buffer at pH 11 showed that about 90 per cent. of the material moved as a single peak for all preparations but at lower ionic strengths the patterns exhibited the peculiarities described by Gillespie (1956).

α-Keratose was prepared by oxidizing wool with peracetic acid and extracting with 0·3N ammonium hydroxide. The extract was dialysed against water to remove γ-keratose and ammonia, precipitated with a few drops of concentrated hydrochloric acid, and the precipitate redissolved in dilute borate (pH 9). All protein stock solutions were kept in the frozen state until required as freeze-drying has been found to affect their physical properties (O'Donnell and Woods 1956*c*).

(ii) *Reagents.*—A.R. salts were used in the preparation of all buffer solutions. Pure sodium dodecyl sulphate was prepared by the method of Dreger *et al.* (1944) from Eastman Kodak dodecyl alcohol. Heavy metal ions were removed from urea by passing a solution through a mixed-bed ion-exchange column and recrystallizing from distilled water as recommended by Kay and Edsall (1956). Guanidine hydrochloride was recrystallized from methanol as described by Kolthoff *et al.* (1957).

(b) *Methods*

(i) Angular light scattering of the protein solutions was measured at 546 mμ using a Brice-Phoenix photometer (1000 series) with the cylindrical cell described by Witnauer and Scherr (1952). In general, the protein solutions and solvents were clarified by centrifuging in a Servall centrifuge at 24,000 *g* for 1 hr followed by filtration under gravity through a sintered-glass filter (porosity No. 4) directly into the light scattering cell. In some of the experiments clarification was achieved more readily by filtration through a Millipore HA filter as suggested by Kay and Edsall (1956).

(ii) The refractive index of each solvent was measured by means of an Abbé refractometer. The refractive index increments of the protein solutions were measured by a differential refractometer of the type described by Cecil and Ogston (1951). With 10M acetic acid and 8M urea solutions it was necessary to smear the edges of the refractometer cell with silicone grease and to seal both inside and outside compartments with a glass plate to prevent creep of the solutions.

(iii) Viscosities were measured at 25±0·01 °C in Ostwald capillary viscometers with times of flow of water of about 200 sec. Intrinsic viscosities $[\eta]$ were obtained by extrapolation of the reduced viscosity η_{sp}/c to zero concentration, where η_{sp} is the relative viscosity of the protein solution and c its concentration in g/100 ml.

The ultraviolet absorption curves were measured by means of a Beckman DU spectrophotometer.

(iv) The protein solutions were prepared for measurements by dialysis for 48 hr at 2 °C against two changes of the appropriate solvent. Different batches of protein were characterized by their nitrogen content (determined by the Kjeldahl semimicro method), and their extinction coefficients at 278 mμ for SCMK2 and 276 mμ for α-keratose. These quantities were referred to the dry weights of the protein solutions. Dry weights were determined after dialysis by drying 10 ml aliquots of the protein solution and dialysate in an air oven at 105–110 °C for 18 hr.

III. Results and Discussion

(a) *Phosphate Buffer pH 6·7, Ionic Strength 0·2*

(i) *Nitrogen Content, Ultraviolet Absorption, and Refractive Index Increments.*—Table 1 shows the values obtained for these quantities for several different preparations of SCMK2, and for α-keratose. The nitrogen contents and refractive index increments for SCMK2 do not show a great variation among batches and a mean value of $16\cdot7_5$ per cent. for the nitrogen content and 0·00190

Table 1

Constants of SCMK2 and α-keratose in phosphate-sodium chloride, pH 6·7 and ionic strength 0·2

Protein Preparation	Nitrogen Content (%)	$E^{1\%}_{1\ cm}$ *	d*n*/d*c*
SCMK2			
Z30F	$16\cdot8_9$	$8\cdot7_4$	0·00190
Z45F	$16\cdot5_6$	$8\cdot7_1$	0·00189
Z54F	$16\cdot8_4$	$9\cdot0_3$	0·00191
Z63F	$16\cdot8_2$	$9\cdot2_6$	0·00189
Z63FP2† ..	$16\cdot8_2$	$9\cdot6_9$	0·00191
Z74F	$16\cdot6_4$	$8\cdot7_9$	0·00188
α-Keratose			
B102	$16\cdot4_9$	$9\cdot2_2$	0·00184
C13	$16\cdot5_8$	$9\cdot0_3$	0·00180

* The extinction coefficients were measured at 278 mμ for SCMK2 and 276 mμ for α-keratose.

† A subfraction of Z63F prepared by ammonium sulphate precipitation (Gillespie 1957). The subfraction gave two descending peaks on electrophoresis in glycine-sodium hydroxide buffer at pH 11·0 in contrast to the original, Z63F, which gave only one.

for d*n*/d*c* was used in all further calculations involving dilute buffer solutions. For α-keratose the values $16\cdot5_5$ per cent. for the nitrogen content and 0·00182 for d*n*/d*c* were used. There is, however, a significant variation in the extinction coefficients of different batches of both SCMK2 and α-keratose indicating non-reproducibility in the preparative procedures since the original wools have almost

identical amino acid compositions. In the case of SCMK2 the variation in extinction coefficients could be due to binding of iodoacetate or thioglycollate both of which absorb in this region. The higher extinction of the ammonium sulphate precipitate of SCMK2 is in accord with the findings of Gillespie (1957). Figure 1 compares the ultraviolet absorption curves of SCMK2 and α-keratose. The curve for SCMK2 is typical of proteins, whereas that for α-keratose does not show such a pronounced maximum in the region 277–280 mμ. The ultraviolet absorption curve for α-keratose in Figure 1 is for preparation C13; another batch prepared in an identical way showed a much less pronounced maximum.

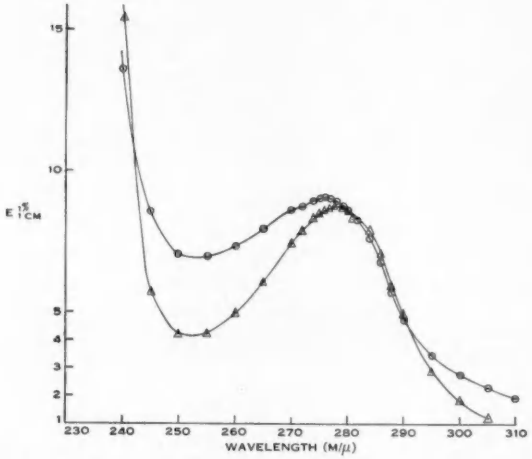

Fig. 1.—Ultraviolet absorption curves showing extinction coefficient ($E^{1\%}_{1\,cm}$) as a function of the wavelength (mμ) for wool proteins at pH 6·7 in 0·2 ionic strength phosphate-sodium chloride buffer.

⊙ α-Keratose. △ SCMK2.

This indicates considerable modification of groups which are responsible for the protein absorption curve in this region. It has been shown that oxidation of proteins with performic or peracetic acid causes modification of tryptophane and methionine residues in addition to oxidizing the —S—S— bonds of cystine to cysteic acid (Alexander, Hudson, and Fox 1950).

(ii) *Light Scattering and Viscosity Measurements.*—It has been shown previously that viscosities of both SCMK2 and α-keratose are time dependent and that this is accompanied by aggregation (O'Donnell and Woods 1956*a*, 1956*c*). Further investigation of the time dependence by light scattering has shown that a small increase (about 15 per cent.) occurred in the 90° scattering on standing for 72 hr during which time there was a considerable decrease in the viscosity of the solution. To overcome the difficulty of the variation of turbidity with time for each dilution in the determination of molecular weight

by light scattering, a series of dilutions was prepared from the cold stock solution and the scattering at each concentration measured at identical times after bringing to room temperature. The plot of $K_{90}c/R_{90}$ against c for SCMK2 at two different times is shown in Figure 2; these results are typical of those obtained for three preparations of SCMK2, K_{90} is the parameter relating the Rayleigh scattering ratio to molecular weight, c is the concentration in g/100 ml, and R_{90} is the Rayleigh scattering ratio. On dilution the 24 hr curve changes slope and it seems probable that the two curves converge at zero concentration to substantially the same intercept. Although the experimental accuracy at high dilutions is low, most experimental errors (contamination from dust etc.) would lead to a curvature in the downward rather than the upward sense.

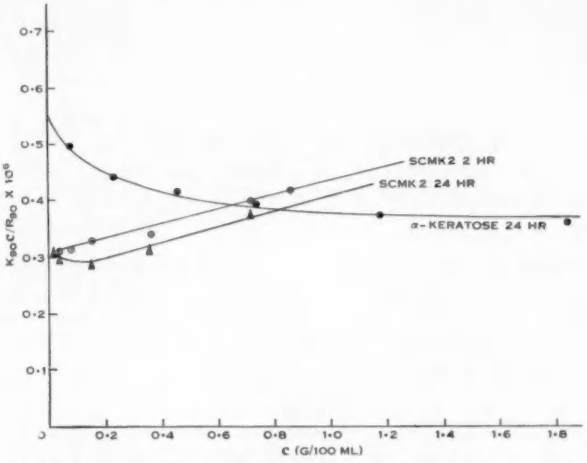

Fig. 2.—Plots of $K_{90}c/R_{90}$ against c for SCMK2 and α-keratose at two different times, at pH 6·7 and ionic strength 0·2.

The results of viscosity measurements carried out in the same manner as the light scattering determinations are shown in Figure 3, which gives the plot of η_{sp}/c against c. In contrast to the light scattering results the viscosity curves at different times diverge at low concentrations so that the extrapolated values of the reduced viscosities are quite different. In order to confirm that the change of slope of the η_{sp} against c curve for 2 hr was a real effect similar measurements were made on two other preparations of SCMK2. The results were similar; in every case at low concentrations the 2 hr curve showed an upward curvature but, after standing for 24 hr this trend, if it existed at all, was very small. O'Donnell and Woods (1956*a*, 1956*c*) explained the decrease of viscosity with time as due to aggregation of the protein to form more symmetrical particles and this was supported by ultracentrifuge experiments on α-keratose which had stood at room temperature for several weeks. The relatively small increase in turbidity (reflecting a change in the weight average molecular weight) suggests

that aggregation must be among the small particles in the solution. This is supported by measurements of dissymmetry (weighted strongly in favour of the larger particles) which show no variation with time or concentration. High dilutions would be expected to inhibit aggregation and this is reflected by the turn up in the reduced viscosity curve and the 24-hr scattering curve. This

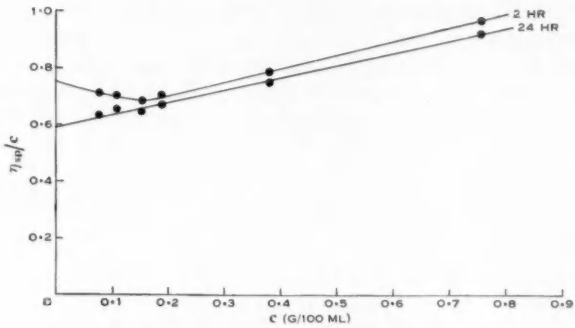

Fig. 3.—Plot of η_{sp}/c against c for SCMK2 at two different times, at pH 6·7 and ionic strength 0·2.

upwards curvature of the light scattering plot is indicative of dissociation on dilution as observed by Doty and Myers (1953) for insulin and Caspary and Kekwick (1957) for fibrinogen. At an ionic strength as high as 0·2 the effect is unlikely to be due to expansion of the molecules as has been found for polyelectrolytes in the absence of salt.

TABLE 2

PHYSICAL PROPERTIES OF SCMK2 IN PHOSPHATE-SODIUM CHLORIDE pH 6·7 AND IONIC STRENGTH 0·2*

Preparation	$[\eta]$	$M \times 10^6$	$Z_{c=0}$†
Z45F	$0{\cdot}52_0$	1·5	$1{\cdot}2_2$
Z54F	$0{\cdot}59_0$	3·0	$1{\cdot}5_0$
Z61–63F	$0{\cdot}40_5$	1·8	$1{\cdot}5_9$

* In determining the physical quantities all dilutions were aged at 25 °C for 24 hr.

† $Z = i_{45}/i_{135}$.

Table 2 gives the intrinsic viscosities, molecular weights, and dissymmetries of three different preparations of SCMK2. There is a wide variability amongst the different preparations and no obvious correlation between the three quantities. This probably reflects different degrees of aggregation during the preparation, the protein being held at 50 °C for 100 min and at room temperature for several days during dialysis and concentration. The sensitivity of the physical properties of these preparations to temperature was demonstrated by

determining their viscosities and 90° scattering after placing in a bath at 50 °C for 20 min and cooling to 25 °C. The 90° scattering increased sixfold and a marked fall occurred in the relative viscosity. The molecular weights of more than 1 million are many times in excess of the value of approximately 200,000 obtained from sedimentation measurements by O'Donnell and Woods (1956*c*).

TABLE 3

EFFECTS OF CENTRIFUGATION ON PHYSICAL PROPERTIES OF SCMK2 (Z54F) IN PHOSPHATE-SODIUM CHLORIDE pH 6·7 AND IONIC STRENGTH 0·2

Centrifuge Data	$[\eta]$	$M \times 10^6$	$Z_{c=0}$
14,000 *g* for 1 hr	$0{\cdot}59_0$	$3{\cdot}0 \times 10^6$	$1{\cdot}5_0$
144,000 *g* for 1 hr	$0{\cdot}62_0$	$1{\cdot}3 \times 10^6$	$1{\cdot}7_0$
144,000 *g* for 3½ hr	$0{\cdot}65_0$	$0{\cdot}95 \times 10^6$	$1{\cdot}7_5$

Since the molecular weights were calculated from the sedimentation coefficient of the main peak of the ultracentrifuge pattern the higher values obtained by light scattering indicate the presence of extremely large aggregates. These larger particles could be observed sedimenting to the bottom of the cell in the early stages of ultracentrifugation.

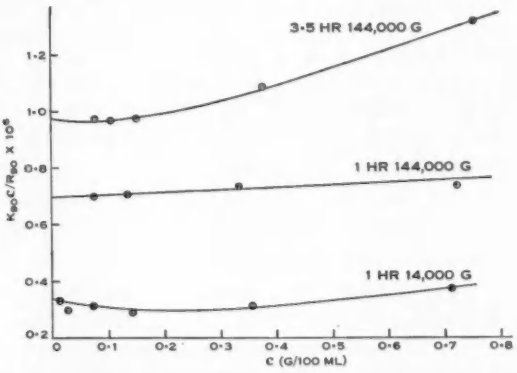

Fig. 4.—Effect of time and speed of centrifuging on the plot of $K_{90}c/R_{90}$ against c, at pH 6·7 and ionic strength 0·2.

An attempt was made to remove these large aggregates by centrifuging one preparation in a Spinco Preparative ultracentrifuge (Model L) at 144,000 *g* for 1 hr and 3½ hr at 0 °C. The supernatant layer was decanted after freezing the bottom of the centrifuge cell in a mixture of ethanol and dry-ice, filtered through a sintered disk (No. 4) under gravity, and each dilution aged at 25 °C for 24 hr. The results shown in Table 3 and Figure 4 indicate a progressive decrease in molecular weight with increasing time and speed of centrifuging together with an increase in the dissymmetry and intrinsic viscosity. This confirms the idea

that aggregation leads to more symmetrical particles. It is clear from Figure 4 that even after the removal of larger aggregates there are indications of further dissociation of the remaining material on dilution. This is also consistent with the viscosity data at the higher dilutions shown in Figure 3. Time effects in viscosity and light scattering measurements on solutions immediately after centrifugation were of the same order after centrifuging at 144,000 *g* as at 14,000 *g* notwithstanding the decrease in molecular weight. If the initial aggregation to form these large particles had occurred at room temperature then we would expect the time effect during restoration of equilibrium to be greater after their removal. It is therefore probable that the initial aggregation occurred at higher temperatures during the extraction of the protein. This would account also for the variability between different preparations.

The behaviour of α-keratose was similar in most respects to that of SCMK2. The light scattering plot for a solution which had been at 25 °C for 24 hr (Fig. 2) showed even greater dissociation on dilution than that for SCMK2. The preparation used had the following constants: $M=1{\cdot}8\times10^6$; $Z=1{\cdot}35$; $[\eta]=0{\cdot}340$. The time dependence of the viscosity was greater than for SCMK2 and the turbidity showed a 10 per cent. increase on standing for 18 hr. These results for α-keratose are at variance with those reported by Alexander and Hudson (1954) and Alexander (1956), who reported values of 62,000 for the molecular weight and 1·0 for the dissymmetry. Since the latter author does not state the experimental conditions under which measurements were made comparison between the two sets of values is impossible. The effect of heat (50 °C for 20 min) on α-keratose solutions at pH 7·0 caused a decrease in the relative viscosity at 25 °C but, in contrast to SCMK2, no change in turbidity. O'Donnell and Woods (1956) reported that the viscosity of α-keratose increased on heating to 50 °C at pH 6; however, at pH 6·7 in the phosphate-sodium chloride buffer we have found that the viscosity always decreases.

TABLE 4

PHYSICAL PROPERTIES OF SCMK2 (PREPARATION Z72F) IN GLYCINE BUFFER AT pH 10·5

Ionic Strength	$[\eta]$	M	$Z_{c=0}$
0·01	$0{\cdot}60_2$	400,000	1·3
0·20	$0{\cdot}34_5$	450,000	1·7

(*b*) *Alkaline Buffers*

In view of the results of O'Donnell and Woods (1956*c*) and Harrap (1955, 1956), which suggest the disaggregation of SCMK2 as the pH is raised, the light scattering and viscosity of SCMK2 solutions were measured at pH 10·5 in glycine-sodium hydroxide-sodium chloride buffer at ionic strengths of 0·20 and 0·01. The molecular weights (Table 4) corrected for dissymmetry are 450,000 at 0·2 ionic strength and 400,000 at 0·01 ionic strength indicating considerable disaggregation at the higher pH. All data were obtained on

solutions which had aged for 24 hr. Although the molecular weights are similar at the two ionic strengths there is a difference in the behaviour of the solutions in that the dissymmetry at 0·2 ionic strength is greater than at 0·01 ionic strength. These values may be contrasted with the intrinsic viscosity (Table 4), $[\eta]$ at pH 10·5 ionic strength 0·2 is less than at 0·01 ionic strength. At first sight the variations in the values of $[\eta]$ and Z with environment appear to be contradictory in terms of the length of the particles. However, whereas the dissymmetry gives a measure of the lengths of the particles, the intrinsic viscosity is determined by both the axial ratio and the solvation of the macromolecules. Furthermore, in a polydisperse system the z-average for dissymmetry and the viscosity average are considerably different. In the system under consideration it is almost impossible to separate all these factors.

At both ionic strengths heating at 50 °C for 20 min and cooling to 25 °C caused a marked fall in the relative viscosity similar to that observed at pH 6·7. At the lower ionic strength the turbidity increased about 2·5 times but at the higher ionic strength there was no significant change after heating.

TABLE 5

PHYSICAL PROPERTIES OF SCMK2 IN DISSOCIATING AGENTS

Solvent	dn/dc	$[\eta]$	M	$Z_{c=0}$
0·2 *I* phosphate-sodium chloride pH 6·7 +0·5 g NaDDS*/g protein	0·00166	$0·11_5$	142,000 (complex) 95,000 (protein)	1·0
10M Acetic acid	0·00163	$0·68_2$	95,000	1·8
8M Urea, 0·2 *I* phosphate-sodium chloride pH 6·7	0·00143	$0·43_3$	140,000	1·4
6M Guanidine hydrochloride ..	0·00126	$0·45_0$	210,000	1·6

* Sodium dodecyl sulphate.

(*c*) *Dissociating Agents*

Table 5 gives the physical constants of SCMK2 in the presence of various dissociating agents.

(i) *Sodium Dodecyl Sulphate.*—In the presence of sodium dodecyl sulphate (0·5 g/SCMK2) in pH 6·7 and 0·2 ionic strength buffer the molecular weight of the protein-detergent complex was 142,000 and the dissymmetry close to unity (Table 5). Previous observations on the interaction of soluble wool proteins with sodium dodecyl sulphate (O'Donnell and Woods 1956*b*) have shown that this quantity of detergent is virtually all bound to the protein. Hence the molecular weight of the protein part of the complex is 95,000, which is to be compared with the value of 52,000 obtained from ultracentrifuge measurements (O'Donnell and Woods 1956*c*). Since the ultracentrifuge patterns show a slight shoulder on the leading edge of the main peak indicating the presence of heavier material, the light scattering value appears to be in satisfactory agreement with previous values and confirms that in the presence of sodium dodecyl sulphate the large

aggregates are dissociated. It is interesting that even the very large aggregates which contribute largely to the light scattering molecular weight of several millions in aqueous solution are dissociated by detergent and it follows that a considerable part of the observed heterogeneity can be accounted for in terms of aggregation.

There was a marked drop in the intrinsic viscosity after the addition of detergent. In 0·2 ionic strength phosphate-sodium chloride buffer pH 6·7 the value of $[\eta]$ for this batch of SCMK2 (Z45F) was 0·520 and this decreased to 0·115 after the addition of sodium dodecyl sulphate. This compares with the values of 0·383 and 0·109 in the absence and presence of detergent respectively obtained by O'Donnell and Woods (1956*c*) for a different batch of SCMK2 prepared in essentially the same way. The close correspondence of the intrinsic viscosities after the addition of detergent is further evidence that the variability in the physicochemical properties of different preparations of SCMK2 is due mainly to differences in aggregation which occur during its extraction and substitution. Time effects in detergent solutions were very small, in agreement with previous results.

(ii) *10M Acetic Acid, 8M Urea, and 6M Guanidine Hydrochloride.*—The molecular weights in Table 5 must be regarded as upper limits, since these are three component systems and the selective solvation of one of the solvent components should be taken into consideration. The contributions of selective solvation and molecular size to the value of the intercept of the light scattering plot are not known in such systems (Stockmayer 1950; Doty and Rice 1955; Kay and Edsall 1956).

10M Acetic acid was found to be a good solvent for SCMK2, although weaker solutions (<5M) were turbid and glacial acetic acid caused gelation of the protein solutions. The intercept at $c=0$ corrected for dissymmetry would indicate a molecular weight of 95,000 in this solvent. The dissymmetry was constant with dilution at 1·8 indicating extension of the protein molecule in this solvent. The intrinsic viscosity $[\eta]$ was 0·682 in 10M acetic acid as compared with 0·520 in the phosphate buffer and this is consistent with the dissymmetry increase which shows that the molecule, although disaggregated, is more extended.

8M Urea had previously been found to disaggregate SCMK2 to approximately the same degree as sodium dodecyl sulphate (O'Donnell and Woods 1956*c*). Table 5 shows a molecular weight of 140,000 corrected for dissymmetry. The dissymmetry is little different to that in aqueous phosphate buffer pH 6·7 suggesting that there is little change in length on disaggregation. Since the intrinsic viscosity of 0·433 in 8M urea is somewhat lower than in phosphate buffer this probably reflects a change in both solvation and axial ratio. The molecular weight of 210,000 in guanidine hydrochloride indicates that this is possibly not as effective as 8M urea or 10M acetic acid as a dissociating agent.

It should be noted that for the last three solvents the length of the molecule calculated from dissymmetry measurements is somewhat greater than would be expected from $[\eta]$. This discrepancy, which has been noted before for polydisperse systems, is due to the fact that dissymmetry is a z-average property and is weighted much more in favour of the longer particles than $[\eta]$.

IV. Acknowledgments

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SOLUBLE WOOL PROTEINS

II. LIGHT SCATTERING AND VISCOSITY IN FORMIC ACID AND DICHLOROACETIC ACID SOLUTIONS

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Summary

The light scattering and viscosity behaviour of *S*-carboxymethylkerateine 2 (SCMK2) and α-keratose have been investigated in formic and dichloroacetic acids. The viscosity at 25 °C of formic acid solutions of SCMK2 and α-keratose showed a large decrease with time over a period of 4 weeks. On the other hand, no parallel changes in light scattering were observed and no conclusive evidence for peptide bond hydrolysis could be found. Time effects in dichloroacetic acid were negligible. SCMK2, but not α-keratose, behaved as a polyelectrolyte in formic acid, the reduced viscosity increasing at low concentrations an effect which was eliminated by the addition of salt. The effects of salt concentration on the plots of $K_{90}c/R_{90}$ against c for solutions of SCMK2 in formic acid were typical of those for highly charged proteins in aqueous solution. Solutions of α-keratose in formic acid and of both proteins in dichloroacetic acid did not show these effects at low ionic strengths.

The solvents employed did not disaggregate the wool proteins to the same extent as 8M urea, 10M acetic acid, or sodium dodecyl sulphate. Variability of the physical properties of different preparations in the two non-aqueous acids is attributed to varying degrees of aggregation.

I. INTRODUCTION

Previous papers have described the properties of soluble wool protein derivatives over a wide range of conditions in aqueous solutions (O'Donnell and Woods 1956*a*, 1956*b*; Harrap and Woods 1958) and it was established that in suitable environments disaggregation of the protein occurred. The best disaggregating agents proved to be sodium dodecyl sulphate, 8M urea, 6M guanidine hydrochloride, and 10M acetic acid. The lowest values obtained for the molecular weight were in the neighbourhood of 50,000 as determined from sedimentation-viscosity measurements and somewhat higher apparent values when measured by light scattering. These values may be contrasted with the minimum of 9000 measured at the air-water interface (Harrap 1955, 1956, 1957). There are several disadvantages with the disaggregating agents so far investigated. The sodium dodecyl sulphate is easily removed from the ionic complex by dialysis or cooling to low temperatures. With mixed solvents such as concentrated urea or acetic acid solutions the systems are of three components and it is impossible to determine molecular weights by light scattering without a knowledge of the selective solvation of the solvent components (Stockmayer 1950; Doty and Rice 1955; Kay and Edsall 1956).

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It was hoped to overcome these difficulties by the use of such solvents as anhydrous formic acid and dichloroacetic acid which have been used for synthetic polypeptides (Bamford, Elliott, and Hanby 1956 ; Doty, Bradbury, and Holtzer 1956). This paper records the behaviour in anhydrous formic acid and dichloroacetic acid of the two soluble protein derivatives, that is, SCMK2 and α-keratose, studied in Part I of this series (Harrap and Woods 1958).

II. Experimental

(i) Wool protein derivatives, *S*-carboxymethylkerateine 2 (SCMK2) and α-keratose were prepared as described in Part I of this series (Harrap and Woods 1958). Before dissolving in the organic solvent the proteins were dialysed first against running tap water, then against distilled water, and freeze dried.

(ii) Reagents: Formic acid was B.D.H. Analar "anhydrous" quality 98–100 per cent. and was used without further purification. The dichloroacetic acid was B.D.H. laboratory reagent and was redistilled at 0·3 mm pressure to remove fluorescent impurities which were present in some preparations. All salts used were of A.R. quality.

(iii) Light scattering and viscosity were measured as described in Part I. Viscometers with times of flow of 300 sec for formic acid and 90 sec for dichloroacetic acid were used.

(iv) The concentrations of the protein solutions were determined by the semimicro-Kjeldahl procedure using the values for the nitrogen contents in the two proteins given in Part I. Protein concentrations are expressed in g/100 ml.

(v) The refractive index increments in the organic solvents were calculated from those in phosphate buffer by means of the formula given by Putzeys and Brosteaux (1936):

$$dn'/dc = dn/dc + \varphi(n_0 - n'_0),$$

where φ is the partial specific volume of the protein and was taken as 0·715, dn/dc is the refractive increment in phosphate buffer (0·00190 for SCMK2, and 0·00182 for α-keratose) of refractive index n_0 (1·336), dn'/dc is the refractive increment in a different medium of refractive index n'_0. The refractive indices of formic acid and dichloroacetic acid were measured in an Abbé refractometer. Table 1 shows the refractive increments in the solvents used.

Table 1

Refractive increments of the proteins

Solvent	dn'/dc		
	n'_0*	SCMK2	α-Keratose
Formic acid	1·373	0·00164	0·00156
Formic acid-0·1M potassium chloride	1·374	0·00163	0·00155
Formic acid-0·5M potassium chloride	1·378	0·00160	0·00152
Dichloroacetic acid	1·468	0·00096	0·00088
Dichloroacetic acid-0·1M potassium chloride	1·468	0·00096	0·00088

* n'_0 refers to wavelength 546 mμ.

III. Results

The solubility of freeze-dried SCMK2 in a number of organic solvents was tested. Dichloroacetic acid and formic acid were excellent solvents for the freeze-dried material, but the protein was insoluble in formamide, *N*-methylformamide, *NN*-dimethylformamide, ethanol, dioxane, chloroform, and glacial acetic acid. Solution of the protein in formamide, *N*-methylformamide, and *NN*-dimethylformamide could be obtained by dialysing an aqueous solution against successive changes of the solvent, the protein forming a clear gel which

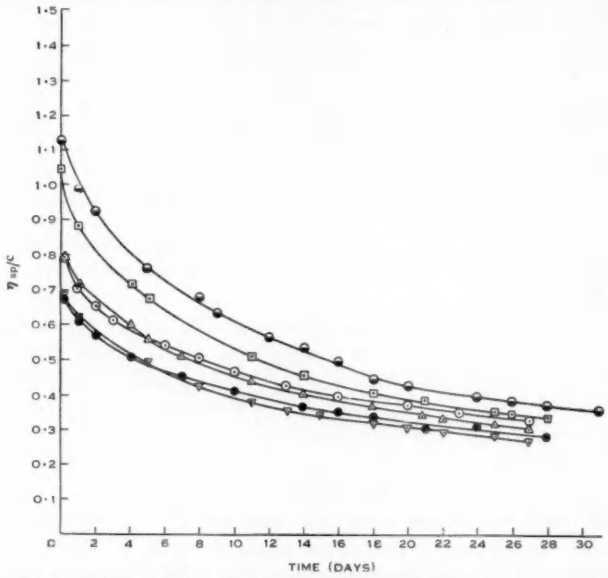

Fig. 1.—Effect of time on the viscosity of SCMK2 (Z68F) in formic acid. ◒ Formic acid and protein 1·70%. ⊡ Formic acid, 0·01M potassium chloride, and protein 1·24%. △ Formic acid, 0·1M potassium chloride, and protein 1·66%. ⊙ Formic acid, 0·5M potassium chloride, and protein 1·56%. ▽ Formic acid, 0·1M potassium chloride, and protein 0·83%. ● Formic acid, 0·5M potassium chloride, and protein 0·78%.

dissolved in excess solvent. Dichloroacetic acid and formic acid were chosen for study because solutions could be readily prepared from the freeze-dried protein, and the protein concentrations of the solutions determined by the Kjeldahl procedure.

(*a*) *Formic Acid Solutions*

(i) A striking feature of solutions of SCMK2 in formic acid was the development of a purple colour on standing at room temperature. In salt-free solutions, the colour developed slowly over a period of 4–5 days, but the addition of potassium chloride to the solvent accelerated the development of the colour which was quite intense after 2 hr. The rate of development of the colour was

greatly reduced by keeping the solutions at 2 °C. Solutions of α-keratose in formic acid on the other hand showed no purple colour even after standing for 4 weeks at 25 °C. Qualitative tests were made with several proteins in formic acid-potassium chloride solutions. Serum albumin, bovine γ-globulin, fibrinogen, lysozyme, egg albumin, urease, and insulin all gave purple colours after standing for 48 hr at room temperature. Gelatin and silk fibroin showed no colour even after standing for several weeks. Josefsson and Edman (1957) noted a purple colour in solutions of lysozyme in formic acid and attributed it to destruction of tryptophane residues. Of the above proteins, with the exception of insulin, all those that give purple solutions contain tryptophane, while silk fibroin and gelatin contain no tryptophane (Tristram 1953). Alexander, Hudson, and Fox (1950) have shown that tryptophane and methionine are destroyed in peracetic

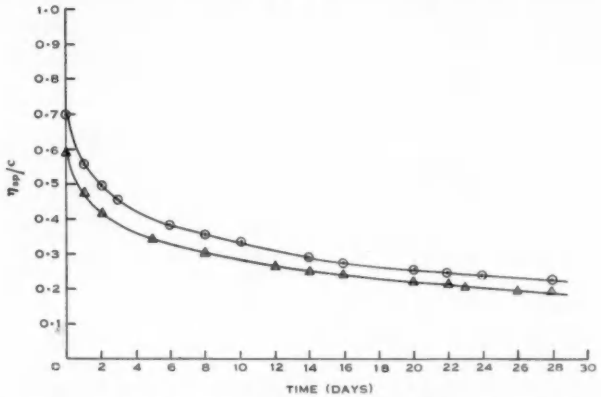

Fig. 2.—Effect of time on the viscosity of α-keratose (B102) in formic acid.
⊙ Formic acid, 0·1M potassium chloride, and protein 1·88%.
△ Formic acid, 0·1M potassium chloride, and protein 0·94%.

acid oxidation, which may account for the absence of colour in α-keratose solutions. The colour in insulin solutions may be due to the presence of impurity, especially as the colour intensity varied with different manufacturer's samples, a most likely contaminant being glucagon, which contains tryptophane (Bromer *et al.* 1956). Bright purple solutions have also been observed during the early stage of acid hydrolysis of wool (Gordon, Martin, and Synge 1941).

(ii) *Viscosity.*—In view of the time dependence of viscosity in aqueous solutions (Harrap and Woods 1958) this factor was investigated in formic acid solutions of SCMK2 and α-keratose. Figures 1 and 2 show the variation of η_{sp}/c with time for SCMK2 and α-keratose at a variety of salt and protein concentrations. It is clear that the variation with time is greater in magnitude and continues for a longer time than in aqueous solutions (Harrap and Woods 1958). The addition of potassium chloride caused a drop in the reduced viscosity and the magnitude of the time dependence became less with increasing amounts of potassium chloride added. It was observed that if the formic acid solutions

were kept at 2 °C for 18 hr then the fall in viscosity was very small. In order to minimize changes of viscosity with time during measurement on a series of dilutions, the freeze-dried protein was dissolved in formic acid, all dilutions made immediately from this solution, and each dilution kept at 2 °C until measurement of its viscosity at 25 °C. The results obtained in this way are designated zero-time values. Figure 3 shows the zero-time plots of η_{sp}/c against c for SCMK2 and α-keratose at several different potassium chloride concentrations. Although different batches of SCMK2 were not identical either in the presence or absence of added salt (Table 2), the upward curvature at low concentrations was

TABLE 2

PHYSICAL PROPERTIES OF WOOL PROTEINS IN FORMIC ACID

Protein Preparation	Concentration of Added Potassium Chloride	[η]		M†	$Z_{c=0}$
		Initial Value	Aged for 4 Weeks*		
SCMK2					
Z68F ..	—	1·60	0·47 (1·70%)	160,000	1·2
	0·01M	0·93	0·31 (1·22%)	—	—
	0·02M	—	—	160,000	1·2
	0·10M	0·57	0·25 (0·83%)	,,	,,
			0·29 (1·66%)		
	0·50M	0·57	0·26 (0·78%)	,,	,,
			0·28 (1·56%)		
Z73F ..	—	1·76			
	0·01M	1·08			
	0·03M	0·85			
	0·10M	0·64		140,000	1·8
α-Keratose					
B102	0·10M	0·49	0·19 (0·94%)	160,000	2·0
			0·20 (1·88%)		
C13	—	0·41			
	0·10M	0·32		80,000	1·4

* The concentrations in parentheses are the concentrations of the solutions which were aged for 4 weeks (Figs. 1 and 2). After 4 weeks, dilutions were made and extrapolated intrinsic viscosities determined.

† Values uncorrected for dissymmetry (see text).

always obtained for SCMK2 solutions in the absence of salt but this did not occur with α-keratose. Table 2 also gives the intrinsic viscosities for SCMK2 and α-keratose solutions which had been kept at 25 °C for 4 weeks at different salt and protein concentrations. After 4 weeks there was still an upward curvature in the η_{sp}/c against c plot for SCMK2 in formic acid with no added salt, although this curvature was less pronounced than at zero time.

(iii) *Light Scattering.*—The purple colour which developed with time in formic acid solutions of SCMK2 generally prevented measurement of any time dependence of light scattering. As the purple colour developed the apparent

dissymmetry values Z rapidly increased to meaningless values of 6 or more. However, for a 0·4 per cent. solution in the absence of added salt there was negligible colour development overnight and during this period there was no change in the intensity of scattered light although in this time the reduced viscosity decreased by more than 10 per cent. Since solutions of α-keratose in formic acid did not turn purple, studies were done on this protein for longer time intervals and at higher protein conentrations.

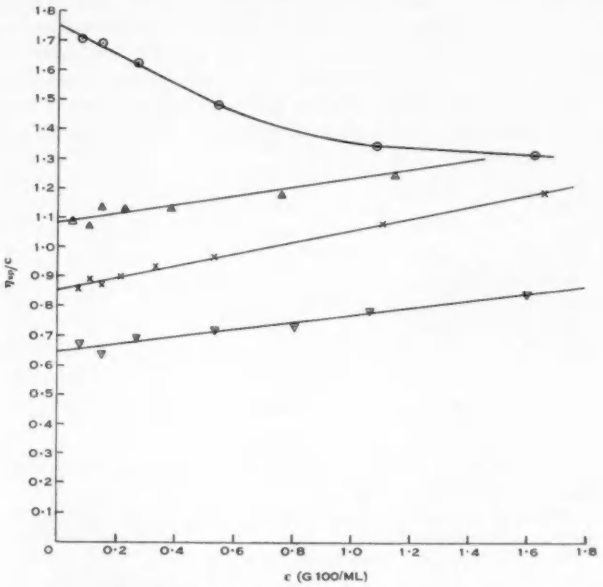

Fig. 3.—Effect of potassium chloride on the plot of η_{sp}/c against c for SCMK2 (Z73F) in formic acid.

○ No salt. △ 0·01M potassium chloride. × 0·03M potassium chloride. ▽ 0·1M potassium chloride.

Some solutions of α-keratose from separate freeze-dried samples of the same batch showed a decrease in turbidity with time, while others showed no time dependence; the equilibrium values all lay on the same $K_{90}c/R_{90}$ against c plot in Figure 4. The most time-dependent solution reached equilibrium in 5 days and thereafter showed no change over the next 14 days; thus there is no parallel with the decrease in viscosity (Fig. 2). It was noted that the preparation which dissolved most slowly in the formic acid-potassium chloride showed the greatest time dependence, suggesting that the state of the freeze-dried protein affects the rate of attainment of true solution. The intercept yielded a molecular weight of 160,000 and a dissymmetry ($c=0$) of about 2·0. Another batch of α-keratose gave a molecular weight of 80,000 and a dissymmetry of 1·4 (Table 2). All the molecular weights quoted are uncorrected for dissymmetry since in many

cases the reciprocal scattering envelope curved down sharply at low angles indicating the presence of very large aggregates in the solution. If a dissymmetry correction were applied to the intercept at zero concentration of the $K_{90}c/R_{90}$ against c plot, the molecular weight would be weighted very heavily in favour of these large aggregates and not characteristic of the solution as a whole since the dissymmetry is a z-average property.

For measurements of SCMK2 in formic acid all dilutions were kept at 2 °C until immediately before measurement to inhibit the development of the purple colouration. Figure 5 shows $K_{90}c/R_{90}$ and dissymmetry plotted as functions of concentration at several different salt concentrations for one batch of SCMK2. The molecular weights and dissymmetries for two preparations are given in Table 2. Despite the variations between different preparations of both SCMK2 and α-keratose, there was no evidence of hydrolytic breakdown as judged from turbidity measurements.

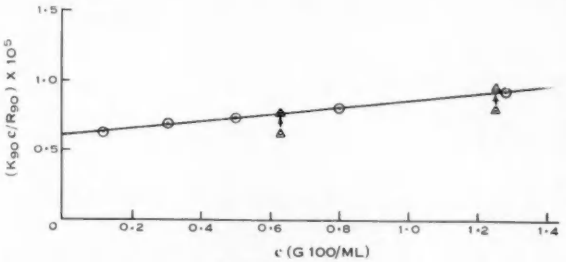

Fig. 4.—Plot of $K_{90}c/R_{90}$ against c for α-keratose (B102) in formic acid and 0·1M potassium chloride.

⊙ Freeze-dried sample which dissolved rapidly. △ Freeze-dried sample which dissolved slowly. Arrows show changes in turbidity with time (see text).

(iv) *Reversal of Formic Acid Treatment.*—A solution of SCMK2 in formic acid was stood at room temperature for 3 weeks and then dialysed against 0·2 ionic strength aqueous phosphate buffer to give a final pH of 6·7. Light scattering and viscosity determinations in aqueous solutions showed that little change had occurred in either property.

(v) *Chromatography.*—Formic acid solutions of SCMK2, bovine serum albumin, gelatin, and fibrinogen, which had stood for 1 month at room temperature, were submitted to chromatography in phenol–ammonia. No spots corresponding to free amino acids were observed, all the material moving with the solvent front with the exception of SCMK2 which showed a very faint unidentified spot with an R_F value of about 0·69.

(*b*) *Dichloroacetic Acid Solutions*

(i) *Viscosity.*—The relative viscosity of dichloroacetic acid solutions of SCMK2 was constant with time with the exception of one preparation which, in the absence of salt, showed a decrease in time of flow for several hours after

placing in the viscometer. The value of $[\eta]$ varies with the preparation of SCMK2 and is lower in the presence of salt (Table 3). Unlike the solutions in formic acid containing no salt, the reduced viscosity-concentration plot was linear with a positive slope. The value of $[\eta]$ for α-keratose was much lower than for SCMK2.

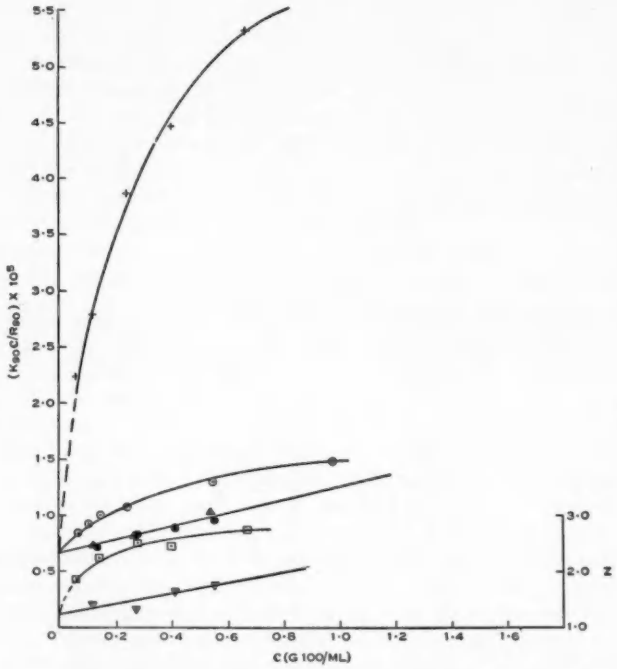

Fig. 5.—Effect of potassium chloride on plots $K_{90}c/R_{90}$ against c and Z against c for SCMK2 (Z68F) in formic acid.

$K_{90}c/R_{90}$: + No potassium chloride. ⊙ 0·02M potassium chloride. ● 0·1M potassium chloride. △ 0·5M potassium chloride.

Z: ⊡ No potassium chloride. ▽ 0·1M potassium chloride.

(ii) *Light Scattering.*—The measurements in dichloroacetic acid solutions were not complicated by development of a purple colour. A slight brown colour was observed in more concentrated solutions but this did not interfere with measurements. Table 3 gives the molecular weights and dissymmetries for SCMK2 and α-keratose in this solvent. Turbidities were independent of time over a period of 24 hr suggesting that no hydrolysis occurred.

TABLE 3

PHYSICAL PROPERTIES OF WOOL PROTEINS IN DICHLOROACETIC ACID

Protein Preparation	Concentration of Added Potassium Chloride	$[\eta]$	M^*	Z
SCMK2				
Z71F	0·1M	0·83	325,000	2·1
Z73F	—	1·32	380,000	2·6
	0·1M	1·03	380,000	1·3
α-Keratose				
C13	0·1M	0·43	82,000	1·0

* Values uncorrected for dissymmetry (see text).

IV. DISCUSSION

(*a*) *Time Effects*

Since solutions of SCMK2 and α-keratose in formic acid showed a large decrease in viscosity immediately after they were prepared, it was important to determine whether this was due to peptide bond hydrolysis by the formic acid, resulting in a decrease in the molecular size of the protein. Light-scattering results suggest that no hydrolysis occurs since a solution of α-keratose in formic acid showed no change in either turbidity or dissymmetry over a period of a week even though the viscosity of the same solution fell by more than 40 per cent. during the same period. The extent of this time dependence of viscosity is typical for both SCMK2 and α-keratose in formic acid (Figs. 1 and 2). Detection of any time effect on the light scattering of SCMK2 in formic acid was made difficult by the development of the purple colour already referred to, but at low protein and salt concentrations its development was sufficiently slow to show that no change in the turbidity or dissymmetry occurred over 24 hr, during which time there was a substantial decrease in the viscosity (Fig. 1).

A further argument against hydrolysis in formic acid is to be found in an experiment in which SCMK2 was stood in formic acid for 2 weeks and then dialysed back to pH 6·7 against 0·2 ionic strength phosphate buffer. The light scattering and viscosity of this solution were almost the same as a similar SCMK2 solution which had not been in contact with formic acid. During the early stages of hydrolysis of proteins by dilute acids free aspartic acid is preferentially released into solution (Blackburn 1950; Partridge and Davis 1950). Solutions of SCMK2 and several other proteins in formic acid which had been kept for 2 weeks at room temperature showed no spot corresponding to aspartic acid on chromatography in phenol–ammonia. The only suggestion of peptide bond hydrolysis was the appearance of additional end-groups (determined by the D.N.P. method) in bovine serum albumin which had stood in formic acid for 2 weeks (Harrap and Woods, unpublished data). Josefssen and Edman (1957) have shown that an N—O acyl shift occurs in solutions of proteins in formic acid.

Upon addition of alkali, reversal may not be immediate so that hydrolysis of the ester bond could take place. The interpretation of the end-group results is therefore inconclusive.

Although there is no change in the dissymmetry of light scattering with time, this does not necessarily indicate the absence of any change in the length of the smaller particles present, since in a polydisperse solution the dissymmetry is weighted heavily in favour of the larger particles. On the other hand, the viscosity is weighted less heavily towards the larger particles so that it is not possible to separate effects due to changes in axial ratio and hydrodynamic volume on the basis of light scattering data for the present systems. Table 2 shows that as the concentration of potassium chloride in the formic acid increases, the fall in $[\eta]$ with time decreases. Moreover, when two solutions of different concentration are aged for the same time, the fall in $[\eta]$ with time is seen to be slightly greater for the more dilute solution. This probably reflects the more rapid attainment of equilibrium in dilute solutions.

The time effects in dichloroacetic acid solutions were not investigated as thoroughly as in formic acid solutions but were negligible in light scattering and of a much smaller order of magnitude than for the formic acid solutions so far as viscosity was concerned. In the ensuing discussion all values for the physical properties of formic and dichloroacetic acid solutions refer to "initial time" values.

(*b*) *Viscosity*

Possibly the most striking feature of the viscosity data in non-aqueous solutions is the shape of the η_{sp}/c against c curve for SCMK2 in formic acid in the absence of any salt (Fig. 3). Instead of the linear relation of positive slope most often found for this plot, the curves turn up sharply at low concentrations in a manner characteristic of aqueous polyelectrolyte solutions (Fuoss and Strauss 1948*a*, 1948*b*). In common with these solutions addition of salt reduces the viscosity of the formic acid-protein solutions and transforms the curves into linear plots. Fuoss and Strauss (1949) showed that a linear plot for polyelectrolyte solutions in the absence of salt could be obtained by plotting c/η_{sp} against $c^{\frac{1}{2}}$. Figure 6 shows that the data for two batches of SCMK2 plotted in this manner approximate to a straight line and the intrinsic viscosities in Table 2 were obtained by extrapolating this plot to zero concentration. The scatter of points about the line in Figure 6 is probably due to the time dependence of the viscosity of the solutions during measurement, particularly at high concentrations. Polyelectrolyte behaviour is not a general property of protein solutions, although Edelhoch (1957) has observed it for denatured pepsin in aqueous solutions under conditions of high charge and low ionic strength and Yang and Foster (1954) suggest it to explain the negative slope of the η_{sp}/c against c curve they obtained for bovine serum albumin at low pH and ionic strength.

Schaefgen and Trivisonno (1951, 1952) have made a detailed study of solutions of polyamides in formic acid. These polymers show a marked similarity to proteins by virtue of the amide linkages along the backbone of the polymer

chain. They have attributed the polyelectrolyte behaviour of these apparently uncharged polymers to the donation of protons to the amide linkages from the formic acid according to the equation

$$-CONH-+HCOOH \rightleftharpoons -CONH_2^+-+HCOO^-.$$

This reaction may also occur in protein solutions in formic acid, but it should be remembered that the positively charged side-chains of the lysine, arginine, and histidine residues will also be partially ionized in this solvent (dielectric constant 58·5) and will contribute to the total net charge.

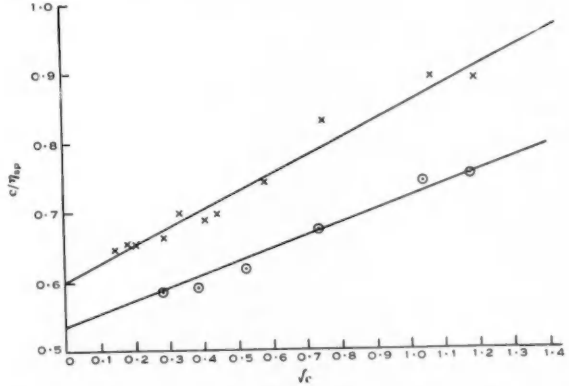

Fig. 6.—Plot of c/η_{sp} against $c^{\frac{1}{2}}$ for two preparations of SCMK2 in formic acid in the absence of added salt.

× SCMK2(Z68F). ○ SCMK2(Z73F).

Table 2 and Figure 3 show that a marked decrease in $[\eta]$ occurs on increasing the potassium chloride concentration of the formic acid solution to about 0·1M, beyond which further additions of potassium chloride have little effect. This salt concentration is somewhat greater than that required to abolish the polyelectrolyte effect in aqueous solutions and is probably due to a reduction in the efficiency of the electrostatic screening effect by neutral salt because of the lower dielectric constant of the solvent.

By contrast with the behaviour of SCMK2 in formic acid, α-keratose gives a linear plot of η_{sp}/c against c both in the presence and absence of salt. Whereas the carboxyl side-chains of SCMK2 would be un-ionized in formic acid, the sulphonic acid residues of α-keratose are probably at least partially-ionized in this solvent, so that the protein would carry less net charge than SCMK2, resulting in the absence of polyelectrolyte behaviour. It is clear from Table 2 that addition of potassium chloride to the formic acid solution leads to a reduction in $[\eta]$, although this reduction is relatively less than for the SCMK2 solutions at similar salt concentrations. This is consistent with the idea that the net charge on α-keratose in formic acid is less than on SCMK2 and is further supported by

the fact that the slopes of the η_{sp}/c against c plots for α-keratose in formic acid are much less affected by salt concentration.

In dichloroacetic acid neither of the wool protein derivatives shows polyelectrolyte behaviour, the plots of η_{sp}/c against c being linear at concentrations below 1 per cent., both in the presence and absence of salt. This probably indicates a lower electrostatic charge on the protein, because of the low dielectric constant of the solvent (*c.* 8). This is also reflected in the slopes of the η_{sp}/c against c plots which were found to be independent of salt concentration. However, Table 3 shows that addition of salt does reduce the intrinsic viscosity of SCMK2 in dichloroacetic acid and also the dissymmetry of light scattering (see below). One cannot decide whether this is due to a reduction in axial ratio, the protein molecule being less unfolded in the presence of salt or to a more general breakdown of the very large aggregates present.

(*c*) *Light Scattering*

The curves of $(K_{90}c/R_{90})$ against c for the single batch of SCMK2 in formic acid studied at several potassium chloride concentrations all appear to extrapolate to the same intercept at zero concentration (Fig. 5), corresponding to a molecular weight of 160,000. As the salt concentration decreases the slopes of the curves increase sharply, a similar effect to that observed by Edsall *et al.* (1950) for bovine serum albumin solutions under conditions of high net charge. This effect has been explained by Doty and Steiner (1952) in terms of electrostatic repulsions producing a non-random system. As with viscosity, a higher concentration of salt is necessary to appreciably lower the slopes of the curves for formic acid solutions than is the case for aqueous solutions. The dissymmetry values are very dependent on concentration and at low ionic strength and high concentration show considerably higher values than those previously reported for protein solutions. There was no evidence of the minimum in the Z against c plots which Doty and Steiner (1952) observed for highly charged aqueous protein solutions at low ionic strength. Plots of $(K_{90}c/R_{90})$ against c and Z against c similar in all respects to those reported above for SCMK2 have been found for formic acid solutions of bovine serum albumin (Harrap and Woods, unpublished data). The molecular weight of the albumin obtained from these results agrees well with that in aqueous solution.

It is evident from the molecular weights in Table 3 that dichloroacetic acid is less effective than formic acid in disaggregating SCMK2.

Considerable variability was observed between different batches of α-keratose as well as between different freeze-dried preparations of the same batch although in the latter instance the variability seems to be a time effect which is entirely eliminated if the solutions are allowed to reach equilibrium. It is interesting that the slopes of the $(K_{90}c/R_{90})$ against c plots for preparation C13 were negative indicating disaggregation on dilution. A molecular weight of about 80,000 was found for this batch in both dichloroacetic and formic acids ; this is comparable to the values found for α-keratose under the best conditions in aqueous disaggregating agents by both light scattering and hydrodynamic methods (O'Donnell and Woods 1956*a*, 1956*b* ; Harrap and Woods 1958).

The dissymmetry values for single batches of both SCMK2 and α-keratose are higher in dichloroacetic acid than in formic acid at 0·1M potassium chloride concentration. This relation is consistent with their intrinsic viscosities in the same solvents and suggests that the proteins are more extended in dichloroacetic acid. However, while the same comparison holds for light scattering in the absence of salt, $[\eta]$ is higher in this case for formic acid solutions than for dichloroacetic acid solutions.

In the foregoing discussion involving comparison of dissymmetry with intrinsic viscosity it should be remembered that the dissymmetry, being a z-average, is not a characteristic of the solution as a whole if the distribution of molecular weights is not the most probable, that is, if the molecular weight averages are not in the ratio $M_z : M_w : M_n :: 3 : 2 : 1$ (Rice and Doty 1957). Solutions of wool protein derivatives in formic and dichloroacetic acids are likely to contain a small number of very large aggregates. This is further illustrated if calculations of the root-mean square end-to-end length $(\overline{r^2})^{\frac{1}{2}}$ of the molecules are made according to the equation of Flory (1953) for random coils

$$\Phi = M[\eta]/(\overline{r^2})^{3/2}.$$

The values $(\overline{r^2})^{\frac{1}{2}}$ so calculated for α-keratose and SCMK2 are much less than those calculated directly from the light-scattering dissymmetry.

(*d*) *General Conclusions*

The variation of physical properties between different preparations of SCMK2 and α-keratose in formic and dichloroacetic acids suggests that complete disaggregation of the proteins in these solvents has not been attained. This presupposes that batch differences are due primarily to differing degrees of aggregation and disaggregation. This seems justified in view of the fact that all batches studied have the same physical properties in urea, sodium dodecyl sulphate, and at the air-water interface (Harrap 1955, 1956, 1957).

The behaviour of the lower carboxylic acids as solvents for synthetic polypeptides has been attributed to the solvation of the peptide backbone, the carboxylic acid acting as both a donor and acceptor in hydrogen-bond formation (Bamford, Elliott, and Hanby 1956).* In addition interaction may take place between the side-chain of the polypeptide and the alkyl group of the carboxylic acid. Doty, Bradbury, and Holtzer (1956) observed complete disaggregation of poly-γ-benzyl *l*-glutamate in dichloroacetic acid and have also attributed the good solvent properties of this acid to hydrogen bonding with the peptide backbone. A similar mechanism of hydrogen bond competition has often been proposed to account for the disaggregating effects of concentrated aqueous urea solution on polypeptides and proteins. Reference to the preceding paper shows that, for wool protein derivatives, 8M urea is considerably more effective in

* As noted earlier Schaefgen and Trivisonno (1951, 1952) have treated polyamides by postulating that, for formic acid at least, an actual donation of proton to the amide link occurs.

promoting their disaggregation than is either formic or dichloroacetic acid, suggesting that hydrogen-bond breakdown is not the only barrier to disaggregation. In the case of the wool proteins studied not only are some of the side-chains very bulky, but many of them carry ionizable groups. Thus in formic and dichloroacetic acids the proteins will bear a net positive charge due to the side-chains of the lysine and arginine residues, while in the aqueous urea solutions studied at pH 6·7 the net charge will be negative. One cannot decide whether the difference in disaggregating efficiency between the non-aqueous acids and the urea solutions is due simply to a difference in charge or whether the presence of water in the urea solutions is important. In this connection it will be recalled that in the preceding paper it was shown that the molecular weight of SCMK2 in 10M acetic acid was less than 95,000, indicating that this concentrated aqueous solution was more effective in disaggregating the protein than either of the two non-aqueous acids. It is also worth noting that the specific laevorotation of the wool proteins is much greater in 8M urea solutions than in either formic or dichloroacetic acids, suggesting that the molecule is more unfolded in the urea solution (Woods, unpublished data).

Finally, it may be said that, except in the case of a single batch of α-keratose, concentrated urea solutions and sodium dodecyl sulphate remain the most effective disaggregating agents for the wool-protein derivatives.

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SHORT COMMUNICATIONS

TORTUOSITY CONCEPTS*

By N. STREET†

It is well known that the application of the Kozeny (1927) equation to the flow of fluids through porous media involves the use of the Kozeny constant k which can be determined from flow measurements. Then since the Kozeny equation as normally derived involves a factor $(L_e/L)^2$, it has been customary to split this constant into two parts, shape factor k_0, and tortuosity $T=(L_e/L)^2$ (Rose and Bruce 1949).

Thus

$$k=k_0T=k_0(L_e/L)^2, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where L_e is the effective fluid flow path length and L the length of the plug packing. T can be obtained from electrical resistivity measurements provided the electrical and fluid flow paths are identical.

There are two concepts concerning the area available for flow, Wyllie and Rose (1950) assuming that it is $A_1=\varphi A$ (A is the cross-sectional area of the plug and φ is the porosity), whilst Cornell and Katz (1953) and O'Connor, Street, and Buchanan (1954), following the Slawinski (1926) concept,‡ assume that it is $A_2=\varphi AL/L_e$.

From Wyllie and Rose's approach, the resistance of a porous medium is $\rho L_e/\varphi A$, and since the resistance of a volume of fluid of the same overall dimensions is $\rho L/A$, hence

$$\begin{aligned} F&=(\rho L_e/\varphi A).(A/\rho L)\\ &=(1/\varphi).(L_e/L), \end{aligned}$$

or

$$(F\varphi)^2=(L_e/L)^2. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

From the Cornell and Katz approach, because the resistance of the porous medium is $\rho L_e^2/\varphi AL$ it follows that,

$$F\varphi=(L_e/L)^2, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where F is the " formation factor ", that is, the ratio of the resistivity of a porous

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‡ Slawinski's approach is, the volume of pore space can be given either by multiplying the volume of the plug by its porosity (i.e. $LA.\varphi$) or by multiplying a hypothetical pore area A_2, by a hypothetical pore length L_e, thus, pore volume is

$$LA.\varphi=L_eA_2,$$

that is,

$$A_2=\varphi AL/L_e.$$

medium saturated with an electrolyte solution, to the resistivity ρ of the electrolyte solution.

Wyllie and Gregory (1955) concluded after extensive experimental work that $(F\varphi)^2$ is preferable to $F\varphi$ as a measure of tortuosity since less variation then occurs in their calculated shape factor.

However, their approach is inconsistent since the comparison should not be between tortuosity as calculated by $F\varphi$ and tortuosity as calculated by $(F\varphi)^2$, but rather between the concepts of $A_1=\varphi A$ and $A_2=\varphi AL/L_e$. Now if either of these concepts is used in determining tortuosity from electrical measurements then the same concept should be used in the derivation of the Kozeny equation.

Thus in the derivation given by Wyllie and Spangler (1952 ; see also Carman 1948) the fluid velocity through a porous medium u_e is greater than the approach velocity u, because the actual path length is greater than the plug length in the ratio L_e/L, and the pore area is less than the cross-sectional area either in the ratio A_1/A or A_2/A.

If the area is A_1 then

$$u_e=u(A/\varphi A)(L_e/L)=(u/\varphi)(L_e/L), \quad \ldots\ldots\ldots\ldots \quad (4)$$

whilst if the area is A_2 then

$$u_e=u(AL_e/L\varphi A)(L_e/L)=(u/\varphi)(L_e/L)^2. \quad \ldots\ldots\ldots \quad (5)$$

From equations (4) and (2), Wyllie and Spangler show that the equation for the approach velocity becomes

$$u=(\varphi m^2/k_0)(P/\eta L)(L/L_e)^2. \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

On the other hand, using the concept that $A_2=\varphi AL/L_e$ in the Wyllie and Spangler derivation gives as the final equation,

$$u=(\varphi m^2/k_0)(P/\eta L)(L/L_e)^3, \quad \ldots\ldots\ldots\ldots\ldots \quad (7)$$

where m is the hydraulic radius, η is the fluid viscosity, and P is the pressure differential causing flow.

We can compare experimental flow results with equations (6) and (7) using electrical measurements to calculate the $(L/L_e)^n$ term by either (2) or (3). Wyllie and Gregory in doing this have used firstly, equation (2) as a measure of $(L_e/L)^2$ and then compared it with (3) as a measure of $(L_e/L)^2$ without in the second case also using the Slawinski concept in the derivation of (5) and (7).

Actually, comparison between (6) and (7) gives a direct comparison between the two concepts $A_1=\varphi A$ and $A_2=\varphi AL/L_e$ thus using the appropriate equation (2) in (6) the $(L_e/L)^2$ can be replaced by $(F\varphi)^2$, on the other hand, use of the appropriate equation (3) in (7) shows that the term $(L_e/L)^3$ should be replaced by $(F\varphi)^{1\cdot5}$.

Hence the true comparison, which must be between the two concepts applied to both derivations, is between $(F\varphi)^2$ and $(F\varphi)^{1\cdot5}$, not between $(F\varphi)^2$ and $F\varphi$.

It is not presently possible to decide finally between the relative merits of the two concepts in the absence of some independent method of determining the shape factor.

An attempt was made by Faris *et al.* (1954) and Faris (1955) to compare measured permeabilities with those calculated from pore-size distributions determined by a mercury injection method; then

$$\text{permeability} = \frac{126 \cdot 6\varphi\overline{r^2}}{(F\varphi)^n},$$

where $\overline{r^2}$ is a function determined by the distribution of pore radii (Burdine, Gournay, and Reichertz 1950).

This comparison indicated that the best agreement between measured and calculated values occurs when the exponent n is between 1·4 and 1·5, thus lending some support to the Slawinski concept.

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THE COMPRESSIBILITIES OF VAN DER WAALS LIQUIDS*

By H. WATTS†

An equation relating the compressibility of a van der Waals liquid to the latent heat of vaporization and the coefficient of thermal expansion is derived from thermodynamics. When certain approximations are made this equation reduces to one previously derived by other authors from the van der Waals equation.

The derivation is based on an equation of pure thermodynamics

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P, \quad \ldots\ldots\ldots\ldots\ldots (1)$$

where T is the absolute temperature, P is the pressure, V is the volume, and E is the internal energy of the liquid. Measurements of $(\partial P/\partial T)_v$ indicate that P is negligible compared with $T(\partial P/\partial T)_v$ for liquids at low pressures and below their boiling points. Further, for a van der Waals liquid

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{\Delta E}{V} v, \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where ΔE_v is the energy of vaporization (Hildebrand and Scott 1950). The enthalpy of vaporization ΔH_v is given by

$$\Delta H_v = \Delta E_v + P\Delta V, \quad \ldots\ldots\ldots\ldots\ldots (3)$$

where ΔV is the volume change on vaporization. The volume of a liquid is small compared to the volume of the vapour. If the vapour is assumed to be an ideal gas, equation (3) approximates to

$$\Delta H_v = \Delta E_v + RT. \quad \ldots\ldots\ldots\ldots\ldots (4)$$

Now

$$\left(\frac{\partial P}{\partial T}\right)_v = -\left(\frac{\partial V}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial P}\right)_T = \frac{\alpha}{\beta}, \quad \ldots\ldots\ldots (5)$$

where the coefficient of thermal expansion

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

and the compressibility coefficient

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

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Substitution of equations (2), (4), and (5) in equation (1) gives, if P is neglected

$$\beta(\Delta H_v - RT)/\alpha V = T. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

Wall and Krigbaum (1949) derived the relations

$$\Delta H_v^2 \beta / V = RT, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

$$\alpha \Delta H_v = R, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

from the van der Waals equation. Substituting equation (8) in (6), the result is

$$\beta \Delta H_v (\Delta H_v - RT)/V = RT. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

If RT can be neglected in comparison with ΔH_v, an assumption not strictly valid, the new equation reduces to that of Wall and Krigbaum (1949), namely, equation (7).

Equation (6) gives about the same degree of correlation of published compressibility data as does equation (7). These equations apply to the differential compressibility at 1 atm pressure. There are insufficient data available in the literature to enable extrapolation of the compressibilities of most liquids to 1 atm pressure; Wall and Krigbaum used values in the range 100–300 atm, and the same values were used in checking the new equation.

Wall and Krigbaum derived equation (7) from a second approximation to the volume of a liquid given by the van der Waals equation, which was considered to be valid only if RT is small compared with the heat of vaporization (Wall 1948). This could account for the difference between their equation (7) and (9). The thermodynamic derivation given in this communication places their equation on a firmer basis.

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THE EFFECT OF HYDROLYSIS ON THE DETERMINATION OF STABILITY CONSTANTS OF FERRIC COMPLEXES*

By D. D. Perrin†

In contrast to the large amount of data on complex formation between ligands and divalent cations, including ferrous ion, relatively few stability constants have been reported for ferric complexes. This is probably because of the greater experimental difficulty in working with ferric ion. Hydrolysis of ferric ion is extensive in all except strongly acid solutions and the solubility of ferric hydroxide is very low (thermodynamic solubility product at 18 °C is 10^{-39}; Cooper 1937). A knowledge of the stability of complexes formed between ferric ion and biological ligands is very desirable if the importance of ferric and ferrous ions in biological systems is to be assessed. For example, such complex formation governs the extent to which the higher-valent iron is stabilized against reduction or precipitation under physiological conditions.

The need to consider hydrolysis in determinations of the stability constants of ferric complexes is evident from results for the ferric glycine system. In an experiment in which the potentiometric titration procedure of Bjerrum (1941) was used, no evidence of complex formation between ferric ion and glycine was found (Albert 1950). Subsequently, spectrophotometric and oxidation-reduction potential measurements showed the 1 : 1 ferric glycine complex to have a log stability constant of 10·0 at 20 °C and an ionic strength of 1·0 (Perrin 1958). This value is higher than for similar glycine complexes with any divalent cation except possibly mercury (Flood and Lorås 1945; Albert 1950; Monk 1951; Perkins 1952).

Hydrolysis of ferric ion gives rise to 1 : 1, 1 : 2, and 2 : 2 ferric hydroxyl complexes with formation constants, obtained from oxidation-reduction potentials, of $k_{1:1}=9\times10^{-4}$, $k_{1:2}=4\cdot9\times10^{-7}$, and $k_{2:2}=1\cdot22\times10^{-3}$, respectively, at 25 °C and $I=3$ (Hedström 1953*a*, 1953*b*). A comparable estimate for $k_{2:2}$ has been obtained from magnetic susceptibility data (Mulay and Selwood 1955). Values of the constants at other temperatures can be calculated by taking the heat content changes for the formation of the 1 : 1 and 2 : 2 complexes as about 10 kcal/mole (Siddall and Vosburgh 1951; Mulay and Selwood 1955; Milburn 1957). In the absence of experimental data the same value has been assumed for the 1 : 2 complex. The formation constants can be corrected to zero ionic strength using the relation:

$$\log k^0=\log k-(\Delta Z^2).f(\gamma),$$

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where ΔZ^2 is the change in the sum of the squares of the ionic charges in the reaction and $f(\gamma)$ is a function of the activity coefficients (Bray and Hershey 1934). If, as appears likely, the ferric hydroxyl complexes are formed by successive loss of protons from hydrated ferric ions, the values of ΔZ^2 for the 1 : 1, 1 : 2, and 2 : 2 complexes are −4, −6, and 0 respectively. From $k^0_{1:1}=5\times10^{-3}$ at 20 °C (Olson and Simonson 1949 ; Siddall and Vosburgh 1951 ; Milburn 1957) and Hedström's (1953*a*, 1953*b*) data adjusted to the same temperature, $f(\gamma)=0\cdot214$ when $I=3$ (sodium perchlorate solutions). Using this value gives $k^0_{1:2}=7\times10^{-6}$ and $k^0_{2:2}=1\times10^{-3}$ at 20 °C. Recent experimental work (Milburn 1957) confirms both the estimated value of $k^0_{2:2}$ and the very small effect of ionic strength on the formation constant of the 2 : 2 ferric hydroxyl complex.

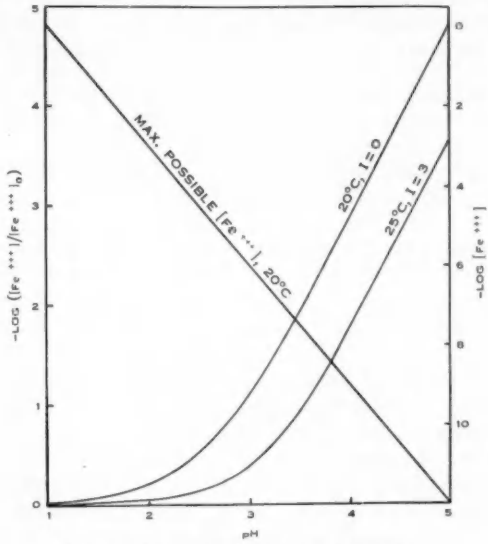

Fig. 1.—Extent of hydrolysis of ferric ion.

From $k^0_{1:1}$, $k^0_{1:2}$, $k^0_{2:2}$ and the solubility of ferric hydroxide (Cooper 1937) it may be deduced that at 20 °C and low ionic strengths all solutions less than 0·002M in free ferric ion contain negligibly small concentrations of the 2 : 2 ferric hydroxyl complex, irrespective of pH. Even allowing a generous estimate of a 1000-fold increase in the solubility of ferric hydroxide in going to 25 °C and $I=3$, formation of the 2 : 2 complex is still negligible under these conditions for concentrations of ferric ion not exceeding 0·001M. These concentrations are of the order of magnitude used by most investigators of metal complex formation.

The extent of hydrolysis of such dilute solutions of ferric ion has been calculated using the appropriate constants (Fig. 1). Temperature effects are relatively small, the main differences between the curves being due to the change in ionic strength. The straight line in Figure 1 provides an estimate of the

maximum free ferric ion concentration which can be present at 20 °C at any pH in a solution of low ionic strength. This line is based on Cooper's (1937) recalculation of the thermodynamic solubility product of ferric hydroxide at 18 °C from oxidation-reduction potential data of Kriukov and Awsejewitsch (1933).

The three commonest methods for studying complex formation with ferric ion are potentiometric (pH) titration, oxidation-reduction potential measurements, and spectrophotometry. In all cases, if reliable values of the successive stability constants, K_1, K_2, . . ., K_x, of ferric ligand complexes are to be obtained it is necessary that over the range of pH studied the total concentration of ferric ligand species should greatly exceed the concentration of ferric hydroxyl complexes. If potentiometric titration is used, and n hydrogen ions are produced for each ion of the complex-forming species, L, which combines with ferric ion, this condition becomes (omitting charges on the ligand and its complexes):

$$n[\mathrm{FeL}]+2n[\mathrm{FeL_2}]+3n[\mathrm{FeL_3}]+\ldots \gg [\mathrm{FeOH^{++}}]+2[\mathrm{Fe(OH)_2^{+}}],$$

that is,

$$nK_1[\mathrm{L}]+2nK_1K_2[\mathrm{L}]^2+3nK_1K_2K_3[\mathrm{L}]^3\ldots \gg k_{1:1}/[\mathrm{H^+}]+2k_{1:2}/[\mathrm{H^+}]^2. \quad \ldots\ldots\ldots\ldots\ldots (1)$$

In using potentiometric titration to investigate ferric complex formation the best experimental approach would seem to be the addition of a possible complex-forming species to a ferric solution, containing mineral acid to repress hydrolysis, followed by titration with alkali. Perchloric acid appears to be the most suitable acid for this purpose because all other common acids form complexes with ferric ion. It has been suggested (Horne 1958) that even with perchloric acid weak complex formation may occur. At low pH values, potentiometric titration becomes insufficiently sensitive; pH 2·5 is near the practical limit. Thus, for a ferric ion concentration of 0·001M, below pH 2·5 the difference between no complex formation and the liberation of one hydrogen ion for every ferric ion present would be masked by an error of less than 0·1 pH unit. On the other hand, hydrolysis increases rapidly as the pH of the solution is raised. Considering both the effect of pH on the sensitivity of the method and the shape of the relevant curve in Figure 1 the most favourable range for observing complex formation appears to be around pH 2·5–3·0. If hydrolysis is not to affect the measured stability constants by more than 10 per cent. we have, for pH 2·5–3·0, at 20 °C and low ionic strengths:

$$nK_1[\mathrm{L}]+2nK_1K_2[\mathrm{L}]^2+3nK_1K_2K_3[\mathrm{L}]^3+\ldots \gg 30 \text{ to } 200. \quad \ldots (2)$$

The higher value is for pH 3. Above pH 3 the necessary minimum for equation (2) is approximately $10^{(2\mathrm{pH}-3\cdot9)}$.

Measurement of oxidation-reduction potentials at high ionic strengths affords a method of obtaining practical stability constants over a wider range than is possible by the potentiometric method. Advantages include reduction of the degree of hydrolysis (Fig. 1), lack of dependence of sensitivity of the

method on pH, and the ability to use higher ligand concentrations. At 20 °C and $I=1$, equation (**2**) becomes approximately:

$$K_1[L]+K_1K_2[L]^2+K_1K_2K_3[L]^3+\ldots \geqslant 10(7\times10^{-4}/[H^+]+4\times10^{-7}/[H^+]^2). \quad \ldots\ldots\ldots\ldots\ldots (3)$$

A value of about $1\cdot2\times10^{-3}$ for $k_{1:1}$ (Milburn 1957), obtained under these conditions, was not corrected for the presence of the 1 : 2 complex.

Spectrophotometric determination of stability constants of complexes formed from ferric ion requires that the concentration ratio of ferric hydroxyl complexes to free ferric ion be small. That is, measurements must be made in sufficiently acid solutions and, if necessary, corrections applied to allow for hydrolysis. Otherwise, and for all subsequent ferric complexes arising by stepwise addition of ligand, conditions are similar to those for oxidation-reduction potential measurement.

From equation (**2**) and the ionization constants of glycine, the lowest value of a stability constant, K_1, of a 1 : 1 ferric glycine complex that could be measured accurately by potentiometric titration of an 0·01M glycine solution is about 1×10^{11} at pH 2·5 and 2×10^{11} at pH 3. With further increase of pH this value rises rapidly. As the reported value of K_1 is 1×10^{10} (Perrin 1958), a stability constant would not be obtained under these conditions, in agreement with experiment (Albert 1950). However, at unit ionic strength and a 1M glycine solution, equation (**3**) gives the lowest measurable limit of K_1 obtainable from oxidation-reduction potentials as about $10^{7\cdot9}$ (at pH 2·9) which thus lies well below the experimental value. Also, as the changes in oxidation-reduction potential measure directly the free ferric ion concentration, correction for moderate hydrolysis of ferric ion is easily made.

On the other hand, although the ferric oxytetracycline (" Terramycin ") complexes have log stability constants as low as 9·6, 7·2, and 5·7 respectively, for the 1 : 1, 1 : 2, and 1 . 3 complexes (Albert and Rees 1956), substitution in equation (**2**) of the appropriate quantities for an oxytetracycline concentration of 0·001M gives values ranging from 110 to 600, for pH 2·5 to 3·0, and so confirms that reliable stability constants can be obtained experimentally. Similar calculations, using published values by the same authors, show that under the same conditions hydrolysis is not important for tetracycline and that results for ferric chlorotetracycline (" Aureomycin ") complexes are near the limits set by equation (**2**) over the selected pH range. Also, in all three cases, when a significant fraction of the iron is present as the 1 : 3 ferric ligand complex (above about pH 4·5) the terms on the left-hand side of equation (**2**) increase more rapidly than those on the right-hand side so that hydrolysis becomes progressively less important.

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